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SYNCRUDE ANALYTICAL METHODS FOR OIL SAND AND BITUMEN PROCESSING

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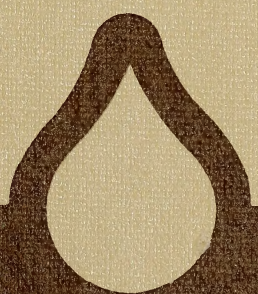

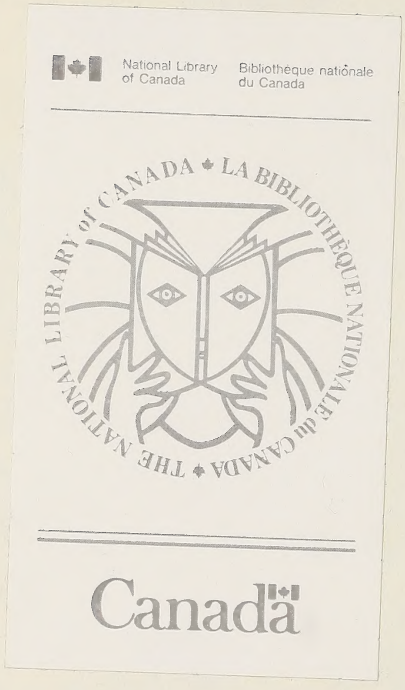
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SYNCRUDE
ANALYTICAL METHODS FOR OIL SAND
AND
BITUMEN PROCESSING

SYNCRUDE CANADA LIMITED
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FOREWORD

The oil sands of northern Alberta have been estimated to contain the equivalent of 600 billion bbl of crude oil. Throughout the world oil sand deposits contain more crude than can be obtained from conventional reserves. It is understandable that commercial interest is now being shown in oil sand hydrocarbons to make up for the dwindling supply of conventional crude. Two things have stood in the way of the use of oil sand hydrocarbons for energy. One is the huge investment needed to construct the industrial facilities needed to recover the oil. Already however the cost of winning conventional crude from distant and difficult sources such as in arctic regions or by deep ocean drilling is making oil sand economically viable and, as conventional crude becomes increasingly expensive, the economics of oil sand will improve.

The second barrier is the technological difficulty of producing a crude from oil sand of a quality sufficient to allow the "synthetic" material to replace conventional crude as refinery feedstock. As found in nature oil sand is an uncongenial mixture of highly viscous heavy oil, water, and siliceous solids, ranging in particle size from sand size grains to fine clays. For deep deposits large quantities of heat must be introduced to render the bitumen fluid, while shallow oil sand must be mined and conveyed to an extraction plant and treated by hot water or solvents. By either route, at some stage the bitumen must be isolated from the other oil sand components and after this must be chemically altered to modify the carbon/hydrogen ratio, reduce the sulphur, nitrogen and heavy metal content, and reduce the molecular weight. Attempts to avoid some of these steps, for instance by direct retorting of whole oil sand without first isolating the bitumen show promise but contain many unknown features.

Overall the technology must allow for production of oil at huge tonnages and within increasingly stringent environmental standards.

As in the case with many recent areas of industrial endeavour the key lies in applied research. Technological development for the oil sand industry has been particularly active in the province of Alberta because of the large Athabasca oil sand deposit — shallow, geographically accessible, relatively rich in bitumen, and close to established conventional oilfields. This development is pursued by the Government of Alberta, the universities, and the oil industry. The Government of Alberta fosters oil sand research by the provision of funding. The agency to assess projects and distribute these funds is the Alberta Oil Sands Technology and Research Authority (AOSTRA). This authority invites and assesses research proposals and offers funds for projects deemed to hold promise.

A leading industrial contributor to oil sands research is the consortium known as Syncrude Canada Limited. Syncrude is a managing company set up to operate a synthetic crude mining and upgrading complex on behalf of the six owning participants:

1. Esso Resources Canada Limited
2. Canada-Cities Service, Ltd.
3. Gulf Canada Resources Inc.
4. Petro-Canada Exploration, Inc.
5. Her Majesty the Queen in Right of the Province of Alberta
6. PanCanadian Petroleum Limited

Ownership changes from time to time as old participants withdraw and new ones enter the consortium. Syncrude early recognised the need for research and set up a Research Department. For years this was the only operating department of the company and was engaged in supplying technical support for the design of the commercial complex. Syncrude is now producing at over 100 000 bpd which is testimony to the degree to which the oil sand technology has already advanced, at least for the shallow mineable regions of the deposit. Research conducted at Syncrude has a pragmatic emphasis since production is the Company's principal interest. Hence improvements to oil sand processing have centered around the hot water extraction process and upgrading of the hydrocarbons so produced to synthetic crude. The company holds over 60 Canadian and over 60 U.S. patents to protect this new technology, and the number grows by about 10 per year in each country. Analytical development has been directed to introducing new methods to provide data for these research programs and also to support the design and operation of the commercial production plants at the Mildred Lake site.

The methods published here are donated by Syncrude as a service to the oil sand industry in general. They have been selected from the total range of Syncrude methods because they are in frequent use and are hence known from experience to serve their purpose; they deal with a cross-section of the total analyses needed in oil sand processing; and, in most cases, they are based upon some novel principle conceived of by Syncrude chemists arising from their experience with the practical problems of analyzing oil sand process streams.

For its part AOSTRA has recognised analytical research as an important feature of oil sand development, and encouraged Syncrude to publish a collection of its analytical methods. The methods in this collection are hence available through a joint effort: they have been invented, developed, and written by Syncrude, and are printed, advertised and distributed by AOSTRA.

Certain general points should be made:

1. The development of analytical procedures for oil sand and related process streams is at an early stage. Syncrude presents these methods in the full knowledge that much development work is required to produce a full range of reliable methods for the oil sand industry.
2. While Syncrude has expended much effort to produce methods that give reliable results, accuracy is not guaranteed to others who use these procedures.
3. While AOSTRA welcomes this volume as a useful step in generating methods that could be a basis for standardization of oil sand analytical procedures, the Authority does not necessarily sanction the methods for general use.
4. Each procedure lists certain safety precautions. The lists are not meant to be exhaustive but are intended to make note of safety requirements peculiar to each method. Normal laboratory safety practice has been assumed in all cases. Toxicity data for bitumen and the numerous hydrocarbon streams generated during processing is currently incomplete. Safety may be ensured by minimizing exposure to these materials.
5. In the description of apparatus, reagents and materials, only information regarding quality or size is provided where many sources of supply exist. For specialized items and major equipment the manufacturer whose product was used is specified. This information is provided only to precisely define our analytical practice and is not necessarily an expression of recommendation. Certain equipment listed is protected by patent and trademark rights. The burden is on the users of these methods to avoid infringing such protection.
6. Relevant methods published by the American Society for Testing and Materials (ASTM), Universal Oil Products, or manufacturers of chemical instrumentation have formed the basis of some of the methods described here. A general acknowledgement is hereby given to these sources: separate acknowledgements are made in the literature references of individual methods.

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OIL SAND AND BITUMEN PROCESSING

In this collection we offer a cross-section of analytical methods used in the Syncrude Research Department for investigating oil sand and bitumen processing. The methods focus on the hot water extraction process, subsequent froth treatment, and bitumen upgrading. Methods are arranged to follow this sequence with the exception of chapters devoted to the analytical themes of sampling and particle size. In order to introduce terminology and present nominal compositions for the sample types identified for analysis, the oil sand and bitumen processing sequence employed by Syncrude is briefly outlined.

Oil sand, water, steam and sodium hydroxide are agitated together to reduce the sand lump size, to separate the bitumen from the sand, and to provide aeration to the freed bitumen. The resulting slurry is passed through a screen to remove any rocks or undigested lumps of oil sand. The material removed by the screen is termed reject. Additional water is added to the screened slurry and the resulting flooded slurry is advanced to a quiescent separator vessel (primary separation). Here the aerated bitumen rises to the surface in the form of a froth. Meanwhile sand particles sink to the bottom and are removed as primary tailings. The central zone of the primary separation vessel is rich in water but also contains bitumen with insufficient buoyancy to form froth, and some suspended solids. This material, denoted as middlings, is advanced to a secondary separation unit where by vigorous agitation and aeration, a second yield of froth is recovered. A second tailings stream, substantially bitumen-free, is removed from the secondary circuit. This process is summarized in Figure 1 and nominal compositions for the extraction streams are given in Table 1.

The primary and secondary froths are combined and naphtha diluent added. The naphtha dissolves the bitumen, to produce a hydrocarbon phase of reduced density and viscosity. The froth, so treated, is centrifuged, first in scroll machines to remove coarse solids, and then in high speed disc machines for removal of fine solids and water. Finally the hydrocarbon product is distilled to remove water, and to recover the naphtha diluent, which can be reused. The residue is a bitumen product substantially free of solids and water. Figure 2 summarizes the froth treatment process employed by Syncrude while Table 2 presents nominal compositions for the process streams.

Although the hot water extraction and froth treatment processes recover bitumen from the oil sands, vigorous upgrading is required to yield products of greater commercial value. This need arises from the physical and chemical properties of bitumen which are summarized in Tables 3 and 4 respectively. Properties of particular note are:

- high content of nondistillable material
- high sulfur and nitrogen content
- high metals content
- high carbon to hydrogen atomic ratio
- high viscosity.

Upgrading is performed in two stages. The first step is fluid coking whose primary function is conversion of the nondistillable bitumen residue to distillable hydrocarbon. In the second step, the naphtha and gas oil distillates from the fluid coker are hydrotreated to reduce the sulfur and nitrogen content, and to increase the hydrogen content. Blending the hydrotreated naphtha and gas oil yields a synthetic crude suitable for current refinery operations.

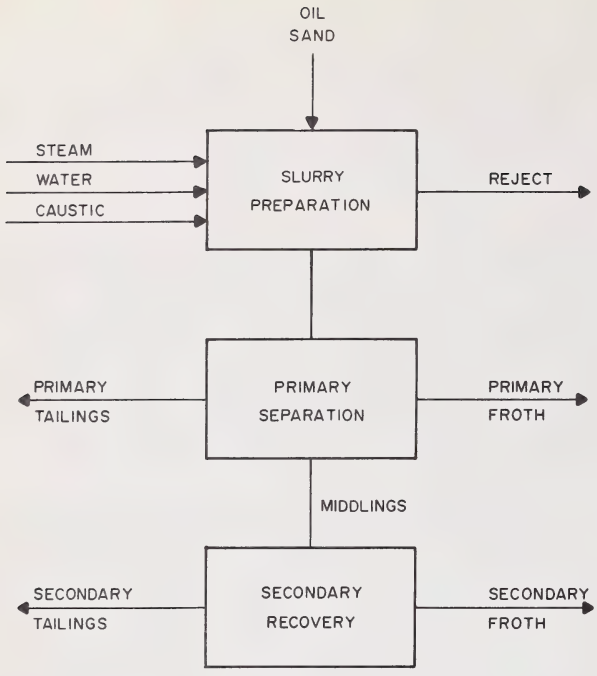


FIGURE 1: BLOCK FLOW DIAGRAM OF THE HOT WATER EXTRACTION PROCESS

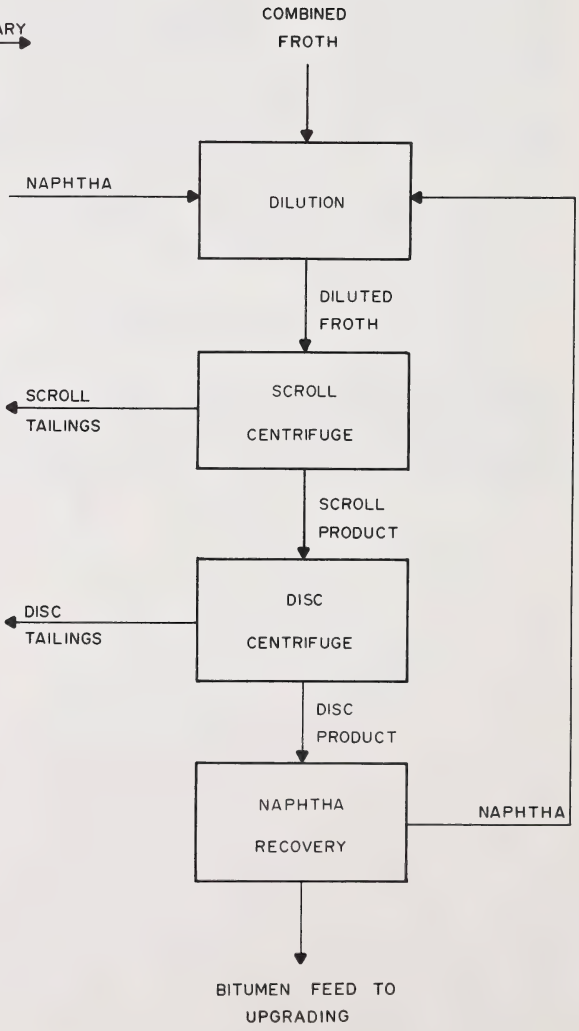


FIGURE 2: BLOCK FLOW DIAGRAM OF THE FROTH TREATMENT PROCESS

TABLE 1
Nominal Compositions of Extraction Process Streams

Stream	Bitumen (wt%)	Water (wt%)	Solids (wt%)
Oil Sand	11.5	4.5	84.0
Slurry	9.0	22.0	69.0
Reject	2.0	10.0	88.0
Flooded Slurry	7.5	42.5	50.0
Primary Froth	66.0	25.0	9.0
Primary Tailings	0.5	34.5	65.0
Middlings	2.5	76.5	21.0
Secondary Froth	23.0	59.0	18.0
Secondary Tailings	0.5	78.0	21.5

TABLE 2
Nominal Compositions for Froth Treatment Process Streams

Stream	Bitumen (wt%)	Naphtha (wt%)	Water (wt%)	Solids (wt%)
Combined Froth	62.0	—	29.0	9.0
Naphtha	—	99.8	0.2	—
Scroll Centrifuge Feed	45.0	27.0	21.0	7.0
Scroll Centrifuge Product	47.0	28.5	21.0	3.5
Scroll Centrifuge Tailings	6.5	4.0	21.5	68.0
Disc Centrifuge Product	60.0	35.0	4.5	0.5
Disc Centrifuge Tailings	5.0	3.0	66.0	26.0

TABLE 3
Typical Physical Properties of Athabasca Bitumen

Specific Gravity	1.012	at 15.6°C
Kinematic Viscosity, mm^2/s	7×10^5	at 15.6°C
	220	at 100°C
Distillation Temperature, °C	IBP	150
	15%	330
	30%	450
	45%	525

TABLE 4
Typical Chemical Properties of Athabasca Bitumen

Elemental Analysis, wt%	
Carbon	83.3
Hydrogen	10.6
Oxygen	0.8
Nitrogen	0.4
Sulfur	4.9
Metals, mg/kg	
Vanadium	250
Nickel	80
Iron	75
Hydrocarbon Type, wt%	
Saturates	20
Aromatics	20
Resins	45
Asphaltenes	15
Molecular Weight, g/mol	600
Conradson Carbon Residue, wt%	13.6

CHAPTER 1

SAMPLE PREPARATION

Most analytical tests are designed to be performed on small quantities of sample. Unfortunately, satisfactory sampling procedures generally result in a first sample too large for direct analysis, which in turn requires that the bulk sample be reduced in size in such a way that the subsample obtained accurately reflects the composition or property of the original bulk material. This can usually be achieved by the sequence of: reducing the particle or lump size (where appropriate); homogenization; and random subsampling. In the case of sensitive or trace components care must be exercised to prevent loss or contamination.

The initial collection of a representative bulk sample from a process stream depends on the flow, composition, and degree of heterogeneity of the stream. Laboratory scale experiments or small pilot plants may allow for a whole stream to be diverted and used as sample. For larger pilot or for commercial-scale operations a further potential source of error is that the bulk sample must itself be collected from a large stream. Heterogeneity of such a stream may be of two types. The stream composition may vary as a function of position within the stream, or may vary as a function of time for a given position within the stream. In response, strategies such as sampling a partial cut some or all of the time, sampling a full cut part of the time, or the preparation of composite bulk samples may be employed. The proper strategy must be decided for each case.

The methods presented in this chapter assume that a representative bulk sample has been taken, and describe subsampling and pretreatment aspects of the analytical sequence. Our studies have shown that one of the most serious sources of error in the analytical results for oil sand and its process streams is improper subsampling. Clearly the multi-component nature of oil sand streams, involving hydrocarbon (often viscous), water, and solids in varying proportions has a complicating influence. In any bulk sample, these fractions are almost always distributed in a heterogeneous fashion. Common approaches used to reduce subsampling errors resulting from inhomogeneity are:

1. selection of a large subsample to ensure adequate representation of the bulk material
2. increasing the number of replicate subsamples analyzed
3. introduction of uniformity into the bulk sample by mixing, blending, emulsion promotion, etc.

The first two of these increase costs by increasing the volumes of reagents and analysis time or by increasing the number of samples analyzed. Consequently, the methods presented in this collection are based on the induction of bulk uniformity to permit representative subsampling.

The subsampling of core retrieved from oil sand reserves requires two steps. In Syncrude practice, 1.5 m lengths of core encased in plastic are submitted to the laboratory. In Method 1.1 the core is cut longitudinally into two slabs to expose a cross-section of the center of the core. One slab is used for geological inspection and from the exposed face of the other a V-notch is cut to obtain a reliable subsample. In our earlier practice, the V-notched sample was then subdivided by the manual chopping, coning, and quartering described in Method 1.2. This has now been replaced by cryogenic grinding (Method 1.3), which is quicker (5 minutes vs 20 minutes); avoids loss of moisture to the atmosphere; and permits better homogenization of core with wide variations in oil content.

In the case of reject (coarse matter removed from the oil sand slurry to prevent it entering the separation vessels) a full stream cut is collected directly onto sample trays during pilot scale operations. It comprises coarse solid matter (chiefly pebbles and undigested lumps of oil sand) with a water and bitumen slurry. In Method 1.4 the bulk reject sample is dried and ground in a hammermill at room temperature to obtain a subsample suitable for analysis.

Bulk secondary froth, which contains mostly bitumen and water is an example of a very heterogeneous fluid. Method 1.5 describes the use of a mechanical shaker to induce bulk uniformity. A subsample is taken by collecting a partial cut as the homogenized mixture is poured. A general method for fluid bulk samples is described in Method 1.6. The bulk sample is collected in a sample vessel fitted with a venturi draft tube. In use the filled vessel is taken to the mixing unit where it is attached to a head that makes the vessel a sealed chamber. A mechanical agitator descends into the bulk sample, driving the components up the centre of the draft tube, round a curved cavity in the head, down the annular space at the outside of the draft tube, round a curved cavity in the base and thence once more past the impeller. With vigorous agitation the sample becomes thoroughly mixed. The analysis-size subsample is withdrawn through a mechanically-operated sample valve. Although some oil sand process streams have an extreme tendency to segregate, the mechanical features of the homogenizer/subsampler give excellent reproducibility. Representative subsamples of 10 to 50 mL can be obtained from 500 to 2000 mL bulk samples after 10 minutes.

Two sample pretreatment methods are described in Methods 1.6 and 1.7. Method 1.6 describes an aqueous extraction of oil sand in order to investigate the soluble ions present. Method 1.7, on the other hand, describes the removal of oil and solids from aqueous process samples in preparation for ion analysis.

Experience has shown that subsampling and sample pretreatment errors are disproportionately large in comparison to analytical errors and may contribute more than 90% of the variability in test results. Proper subsampling of the multiphase streams that arise from oil sand processing is an essential first step in the analytical process.

Sampling of Oil Sand Core for Analytical and Geological Inspection

Scope: This method provides representative samples of oil sand core suitable for laboratory inspection and geological characterization. The method is designed for core encased in a polyvinyl chloride sleeve approximately 1.5 m in length and 64 mm in diameter.

Summary: The core and plastic sleeve are frozen and then sawed to expose the interior of the core and permit removal of a heart-cut sample. The automated sawing operation which uses diamond-tipped saw blades is performed in two steps: slabbing and sampling. Slabbing consists of transverse and longitudinal cuts. The transverse cut provides 0.75 m sections for ease of handling. The sections are then longitudinally sawed in half to expose the interior of the core. One half of the core is washed to eliminate striations and set aside for geological characterization and photography. It also provides a retain suitable for lease development requirements specified by Alberta's Energy Resources Conservation Board. The other half of the core is transferred to the sample saws. Two saws set at 45 degrees cut a V-notch in the exposed core. The oil sand in the V-notch is removed, labelled, and stored at 4 to 5°C to await homogenization and subsampling.

Background: The inspection of vertical core drilled throughout an oil sand deposit provides estimates of the reserves and geological information necessary for mining the oil sand. The core as received from the field is contained in a rigid plastic sleeve. This sleeve forms the inner core barrel during drilling operations and retains the core material. This effectively eliminates handling of the core and ensures consolidation which is required for accurate geological description and sampling. However, the use of the plastic sleeve requires sawing of the sleeve and core in order to expose the core. Due to the numerous steps involved and the large volume of core to be processed, the sawing operation has been automated.

The sawing operation requires that the core be in a frozen state. This requires a temperature of −45°C. Freezing may be accomplished by packing the core in dry ice for 10 to 12 hours. For processing large volumes of core a commercial freezer, which requires only 4 hours storage to freeze the core, is more suitable.

During the drilling operation the outside of the core becomes contaminated with drilling mud and other chemical additives associated with drilling. Samples for analytical inspection must be removed from the center portion of the core to ensure a contaminant-free sample. This is accomplished by a heart-cut or V-notch removed from the slabbed face of the core.

Dehydration of the sample must be prevented. Core drilling is normally conducted during the winter season and the cold temperatures prevent dehydration occurring in the field. However, the core upon arrival at the laboratory must be stored at 4 to 5°C until it is processed. After slabbing and V-notching, the V-notched material is stored at 4 to 5°C to await cryogenic grinding by Method 1.3. The cryogenic grinding provides an analytical-sized sample suitable for laboratory testing.

Safety Considerations: The sawing operation, the handling of frozen materials, and the use of large volumes of water make the use of the following personal protective equipment mandatory:

1. Coveralls, rubber aprons, and rubber boots. Large volumes of water are used as a cooling medium for the slabbing saw blade and for cleaning slabbed sections for geological characterization. This water inevitably sprays, necessitating the use of protective equipment.
2. Heavy-duty rubber gloves to protect hands from cold burns during handling of the frozen core.
3. Hearing protection. Ear muffs or ear plugs are required due to the noise level generated by the saws and the dust collection system.

4. Dust masks. Although the V-notch saw has an efficient dust collection system, core with a high clay content produces sufficient dust that dust masks must be worn.

As housekeeping is a necessary part of a safe work environment, the equipment and floors are washed down each day with varsol and water.

Apparatus, Reagents, Materials:

1. Core transport trays — fabricated from galvanized corrugated sheeting to hold six cores of 1.5 m length and 64 mm outside diameter.
2. Slabbing saw — shown schematically in Figure 1 and including the following features:
   i) 7.5 kW, 58 rev/s motor to drive a 180 mm diameter diamond-tipped blade at 38 rev/s.
   ii) torque control which provides uniform pressure on the leading face of the saw blade in order to reduce wear and breakage of blades.
   iii) water introduced directly onto the blade for cooling and lubrication.
   iv) longitudinal and transverse core supports.
   v) spring-loaded core guide to prevent movement of the core in the longitudinal support.
   vi) spring-loaded core splitter to keep the cut core separated.
   vii) saw carriage equipped with Thompson ball bushings. The carriage moves along two 76 mm diameter ground and polished steel shafts which are protected from dust by flexible rubber boots.
   viii) safety switch in front of the saw carriage to protect the operator by immediately stopping the saw carriage when activated.
3. V-notch saw — shown schematically in Figure 2 and including the following features:
   i) two 1.5 kW Arbor electric motors to drive 250 mm diameter diamond-tipped blades at 57 rev/s.
   ii) torque control which provides uniform pressure on the leading face of the saw blades in order to reduce wear and breakage of the blades.
   iii) saw carriage equipped with Thompson ball bushings. The saw carriage moves along two 76 mm diameter ground and polished steel shafts which are protected from dust and grit by flexible rubber boots.
   iv) core support equipped with core lifting mechanism and core-locking fingers activated by pneumatic cylinders.
   v) dust pick-up head attached to the front of the saw carriage and connected to the dust collection unit by 100 mm ID exhaust hose.
   vi) safety switch in front of the saw carriage to protect the operator by immediately stopping the saw carriage when activated.
4. Core-washing facility — a steel tank 1.2 m x 0.6 m x 0.6 m with an outlet 0.3 m from the bottom. The tank contains an inclined fixture capable of holding a 0.75 m slab of core for washing.
5. Dust collection equipment — model 84 manufactured by Torit Division, Donaldson Corp. Inc., St. Paul, Minnesota. The dust collection unit is modified to permit connection with the dust pick-up head of the V-notch saw carriage using 100 mm ID exhaust hose.

Procedure:

Although the operating procedures for the slab and V-notch saws are detailed separately, the V-notch sawing is performed immediately following the slab sawing. Prior to beginning the sawing operation freeze the core to $-45°C$.

A. Slab Sawing

Preparation

1. Turn on the cooling water to the saw blade, the main power switch, and the power switch on the control panel.

Transverse Cut

2. Place a section of core in the transverse mount, ensuring that it is positioned to be cut in half. Press the START button for the saw and then the FORWARD button for the saw carriage. After the saw has cut the core in half, press EMERGENCY STOP to shut off the saw blade and stop the forward motion of the saw carriage. Press the REVERSE button to return the saw carriage to its starting position.
3. Place one half of the core on the core tray and place the other half in the longitudinal mount.

Longitudinal Cut

4. Press the START button for the saw and then the FORWARD button for the saw carriage. The saw moves forward and commences the slab cut. As the saw moves through the core, the splitter prevents the two halves of the core from freezing together behind the blade. After the cut is complete the forward motion of the carriage is terminated. The two halves of core are lifted out of the mount, ensuring that the two halves are kept apart. One half is placed on a second core tray to await V-notching. The other half is placed in the washing trough, subjected to a strong jet of water to clean the face of the core, and then replaced on the core tray. Press the CARRIAGE RETURN switch to return the carriage to the starting position.

B. V-notch Sawing

5. Turn on the main power switch for the saws, the power switch for the dust collector, and the power switch for the control panel.
6. Activate both saws by pressing the ON switch for each saw.
7. Take the slabbed core, place it in the core support, and press the FORWARD switch. As the saws begin their forward sequence the core-locking fingers which hold the core in place rotate over the core and the core-lifting mechanism presses the core up against the core-locking fingers. In this way the core is firmly held in place and a flat surface is presented to the saws. The saws cut a V-notch section in the core and the angle of cut is such that the section is retained in the core by a 3 mm strip of core. When the V-notch is complete a limit switch stops the forward sequence and releases the core-locking fingers. Remove the V-notched core from the saw and place it on the core tray. Press the RETURN switch to return the saw carriage to the starting position.
8. Remove the oil sand from the V-notch and store in plastic bags at 4 to 5°C.

Calculations: Not applicable.

Precision: Not applicable.

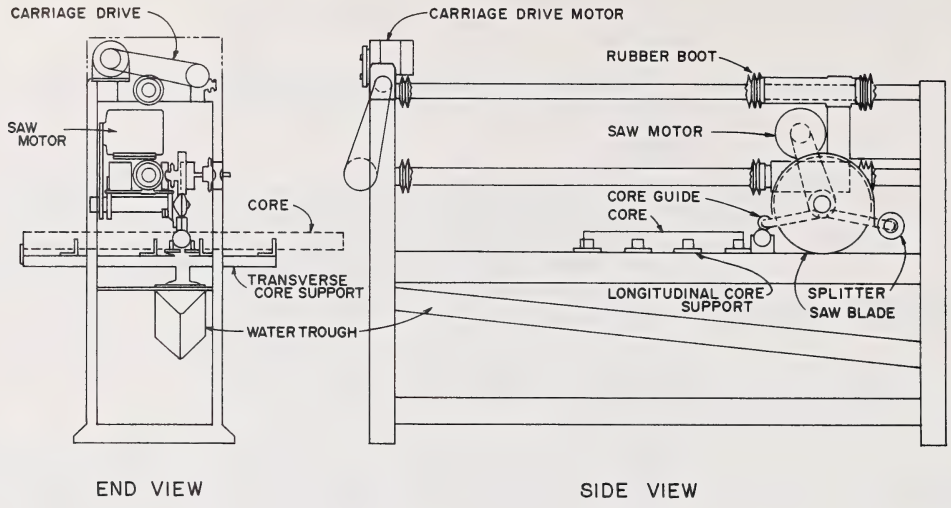


FIGURE 1: SLABBING SAW

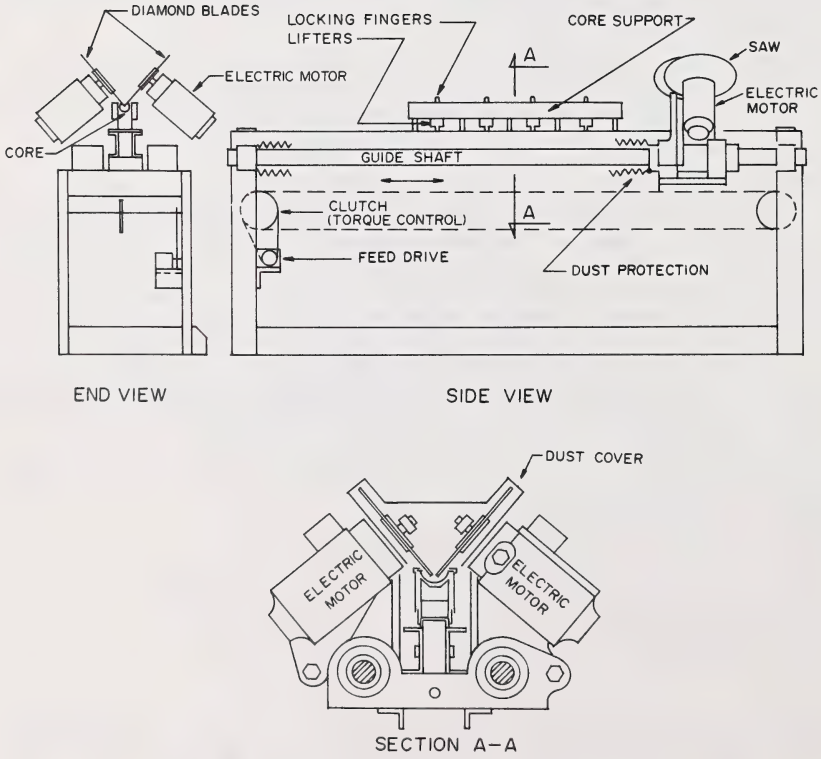


FIGURE 2: V-NOTCH SAW

Subdivision of Bulk Oil Sand Samples

Scope: This method subdivides bulk oil sand samples into quantities convenient for lab analysis.

Summary: The sample is homogenized and subdivided through a sequence of chopping, quartering and mixing procedures.

Background: Homogenization and subsampling are required to prepare oil sand samples for subsequent analysis, e.g. bitumen/water/solids by Methods 2.7 and 2.8.

Significant amounts of water may be lost during the procedure through exposure of subdivided sample to the atmosphere. To minimize the loss, the procedure is performed as quickly as possible.

Oil may be lost from the oil sand by adhering to the surfaces it contacts. However, this loss is not significant compared to the total oil in the sample.

Safety Considerations: No unusual safety considerations.

Apparatus, Reagents, Materials:

1. Polyethylene sheet - approximately 1 m square and 150 μm thickness.
2. Spatula with 300 mm stainless steel blade. A handle welded to the center of the cutting blade facilitates use.
3. Sample bottles - 125 mL.

Procedure:

1. Empty the bulk oil sand sample onto the polyethylene sheet. Remove stones greater than 6 mm in any dimension. Do not confuse stones with clay lumps.
2. Chop the oil sand for a period of time ensuring all particles are less than 12 mm in any dimension. Cone and quarter the mixture. Combine two opposite corners and discard the remainder.
3. Repeat the chopping, quartering and combining procedure twice more. Resultant particles should not exceed 6 mm in any dimension.
4. Transfer approximately 50 g of oil sand (a) from the latter pile to a 125 mL sample bottle and submit for analysis. Store the remaining oil sand in a tightly capped bottle at 4°C if retains are required.

Calculations: Not applicable.

Precision: Not applicable.

Comments:

a. The subsample size is normally selected to provide the optimum amount of sample for bitumen, water and solids determination by Methods 2.7 or 2.8.

Preparation of Composite Oil Sand Core Samples by Cryogenic Grinding

Scope: This method describes the homogenization of oil sand obtained from core samples by means of a hammermill cooled by liquid nitrogen. Although the method was specifically developed for the V-notch section of core samples (Method 1.1), it generally applies to oil sand samples ranging from about 250 g to 2000 g.

Summary: The V-notched sections of core, which are stored in plastic bags, are frozen, broken up with a hammer and covered with dry ice. The V-notched sections are then fed into a hammermill adapted for cooling with liquid nitrogen. The samples are pulverized by the rotating hammers and passed through a 3 mm diameter screen. The finely ground samples are caught in a plastic bag, quickly mixed, and subsamples are poured into bottles for subsequent analysis.

Background: Cryogenic grinding generates pulverized, homogeneous oil sand for subsampling. The circulation of liquid nitrogen through the apparatus ensures temperatures below −45°C and minimal changes in the bitumen, water and solids content. In addition, the fines content is not altered, yielding subsamples suitable for particle size distribution measurements.

This procedure assumes samples are prepared by Method 1.1. Normally the subsamples produced are subsequently analyzed for bitumen, water and solids by Method 2.8 and for particle size distribution by Method 4.3.

Safety Considerations:

1. Insulated rubber gloves must be worn due to the cold temperatures.
2. Dust masks, ear plugs, safety goggles, and coveralls must be worn when operating the hammermill.
3. Varsol — flammable.

Apparatus, Reagents, Materials:

1. Mikro Pulverizer — model 1SI. Ducon-Mikropul Ltd., 1940 Steeles Ave. East, Bramalea, Ont., L6T 1A7. The unit is adapted for cryogenic operation as shown in Figure 1. Features of the apparatus include:
   i) The hammermill is equipped with six Hastellite tipped hammers and a 3 mm diameter stainless steel screen to prevent large lumps of material from dropping through to the receiver.
   ii) Rotary valve and housing connected to the hammermill and the feeder tube. By means of a lever this valve can be closed while loading the feeder tube and then opened after the hammermill has been started to allow the sample to enter the pulverizing chamber. The valve is spring-loaded to ensure the valve only moves to the fully open position to permit easy delivery of the sample into the pulverizing chamber.
   iii) Three lines distribute liquid nitrogen from a manifold situated on the grinder frame. One line cools the support for the sample can. The liquid nitrogen exits from the can support and is used to cool the hopper. A second line cools the feeder tube. The liquid nitrogen exiting from the hopper and the feeder tube, together with a third line, are directed to the pulverizing chamber (Figure 1 does not show these connections). The liquid nitrogen exhausts through the hopper.
2. Liquid nitrogen supply.
3. Stainless steel beakers — 2 L capacity, for use as sample cans.
4. Plastic bags — 280 mm x 460 mm x 0.07 mm.
5. Glass sample bottles — 125 and 250 mL, with screw tops.
6. Varsol.
7. Dry ice.

Procedure: Cooling Grinder

1. Attach the hose from the liquid valve of the nitrogen cylinder to the manifold located on the grinder frame.
2. Commence cooling the grinder by turning on the liquid nitrogen supply.
3. The flow of liquid nitrogen to the feeder tube, hammermill, and can support is adjusted by the manifold valves. Adjust the flow until the liquid nitrogen is flowing steadily through the apparatus. Start the hammermill once or twice while cooling to prevent bearings from seizing.
4. When the machine is cold enough for operation, e.g. less than about $-100°C$, adjust the liquid valve on the cylinder for minimum flow. Approximately 2 hours is required to cool the machine.

Sample Preparation

5. Prior to grinding, the samples are stored in a freezer to ensure a sample temperature below $-45°C$. While the grinder is cooling, the plastic bags containing the V-notched sections are removed from the freezer and the oil sand is broken up with a hammer to facilitate pouring into the feeder tube of the grinder. Samples are then covered in dry ice.
6. Sample bottles of 125 mL and 250 mL capacity are labelled to receive the cyrogenically ground subsamples. Preparation of the sample bottles at this point is necessary since the sample quickly warms up and congeals after grinding.

Operation of the Cryogenic Grinder

7. Take the sample can and put a 280 mm x 460 mm plastic bag into it, fold the bag over the rim of the can, and place the can in the can support.
8. Between samples, the plunger for the feeder tube is normally removed and stored on dry ice. With the lever for the rotary valve in the closed position position, pour the sample into the feeder tube and replace the plunger.
9. Press the START button. Move the lever to the OPEN position. The lever will stop when the spring loaded stopper engages. Using the plunger, ensure the entire sample is passed through the grinder.
10. When the entire sample has been ground, press the STOP button. Pull the plunger back a few inches and lift up the spring loaded stopper. Move the lever to the CLOSED position.
11. Tap the plastic screen a few times to remove any sample caught in the screen and then remove the sample can. Pull the bag out of the sample can, shake the bag to mix the sample, and pour subsamples into the 125 mL and 250 mL sample bottles. The 125 mL bottle is filled approximately 1/3 full and submitted for bitumen, water, and solids determination by Method 2.8. The 250 mL subsample may be used as a retain or for particle size distribution measurements.
12. Steps 7 to 11 are repeated for each sample.

Shutdown

13. When grinding is completed, turn off the liquid nitrogen supply and allow the apparatus to warm to room temperature.
14. Remove the plunger from the feeder tube and clean with Varsol.
15. Disconnect the cooling lines to the feeder tube, hammermill housing and can support. Disconnect the feeder tube from the rotary valve housing and clean it with Varsol.
16. Remove the rotary valve and thoroughly clean it and the housing with Varsol.

17. Remove the clamp from the hammermill cover and tilt the cover forward. Remove the stainless steel screen and clean it with Varsol. If the screen has been damaged, replace it with a new screen.
18. Clean the hammers and chamber with Varsol.
19. Remove the woven plastic screen and can support. Immerse them in Varsol for a thorough cleaning.
20. Reassemble the apparatus.

Calculations: Not applicable.

Precision: Not applicable.

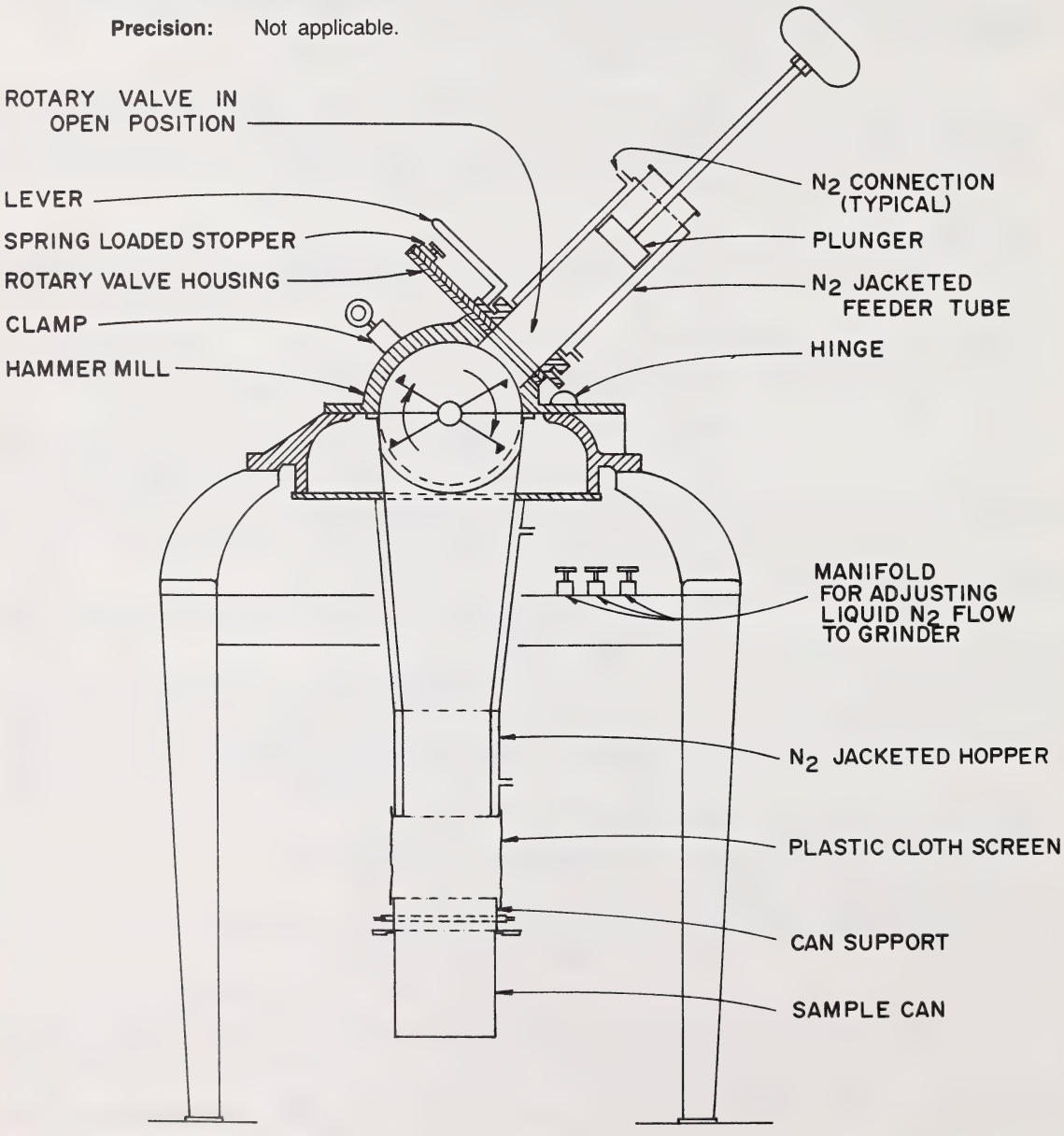


FIGURE 1 CRYOGENIC GRINDER

Preparation and Subdivision of Bulk Reject Samples

Scope: This method prepares and subdivides bulk reject samples into quantities convenient for analysis.

Summary: Reject samples are dried to facilitate homogenization and the weight loss is recorded. The sample is then pulverized in a hammermill.

Background: Reject is a very heterogeneous material. The sampling and subdivision described herein should be considered only as the best procedure currently available for process study.

This method is designed for use with a pilot scale operation in which 2-4 kg samples are collected directly on the trays used to dry the samples.

The weight loss on drying is calculated as a water loss. However the drying procedure cannot distinguish between water and volatile organic material.

Safety Considerations:

1. Safety glasses must be worn when the hammermill is in operation.
2. Do not overload the hammermill.
3. Allow the hammermill to come to a complete halt before removing sample or reloading the hopper.

Apparatus, Reagents, Materials:

1. Drying oven — forced draft, set at 120°C. Dimensions of the oven must be sufficient to contain reject trays described below.
2. Asbestos gloves.
3. Spatula — 100 mm wide stainless steel blade.
4. Hammermill — 7.5 kW, 30 rev/s, with flat blades. The hammer housing has an internal diameter of 355 mm and the feed spout is equipped with a pan type feeder designed to prevent backfiring of rock material. In either the up or down position there is a seal between the grinding section of the mill and the operator. Forty hammers made of austenitic manganese steel are used (see Figure 1).
5. Reject trays — 380 x 400 x 40 mm made from aluminum of approximately 2.5 mm thickness.
6. Sample bottles — 125 mL.

Procedure:

1. Collect a 2-4 kg bulk reject sample in a reject tray.
2. Weigh the reject tray and "wet" sample. Dry in the oven at 120°C for 4 hours.
3. Remove reject tray from the oven and allow to cool for 1 hour. It is good practice to dislodge and loosen the sample from the tray while it is still warm. Weigh the reject tray and "dry" sample.
4. Pulverize the sample in the hammermill, collecting the product in a pail. Stir the crushed sample to ensure homogeneity.
5. Take a suitable subsample (e.g. 30 g for bitumen/water/solids by Method 2.8) of the homogeneous powder and place it in a 125 mL sample bottle.
6. Weigh the empty reject tray.

Calculations: Calculate the % H_2O loss with the following equation:

$$\% \ H_2O \ loss = \frac{A - B}{A - C} \times 100$$

where: A = weight of tray plus "wet" sample, g
B = weight of tray plus "dry" sample, g
C = weight of empty tray, g

Precision: Not applicable.

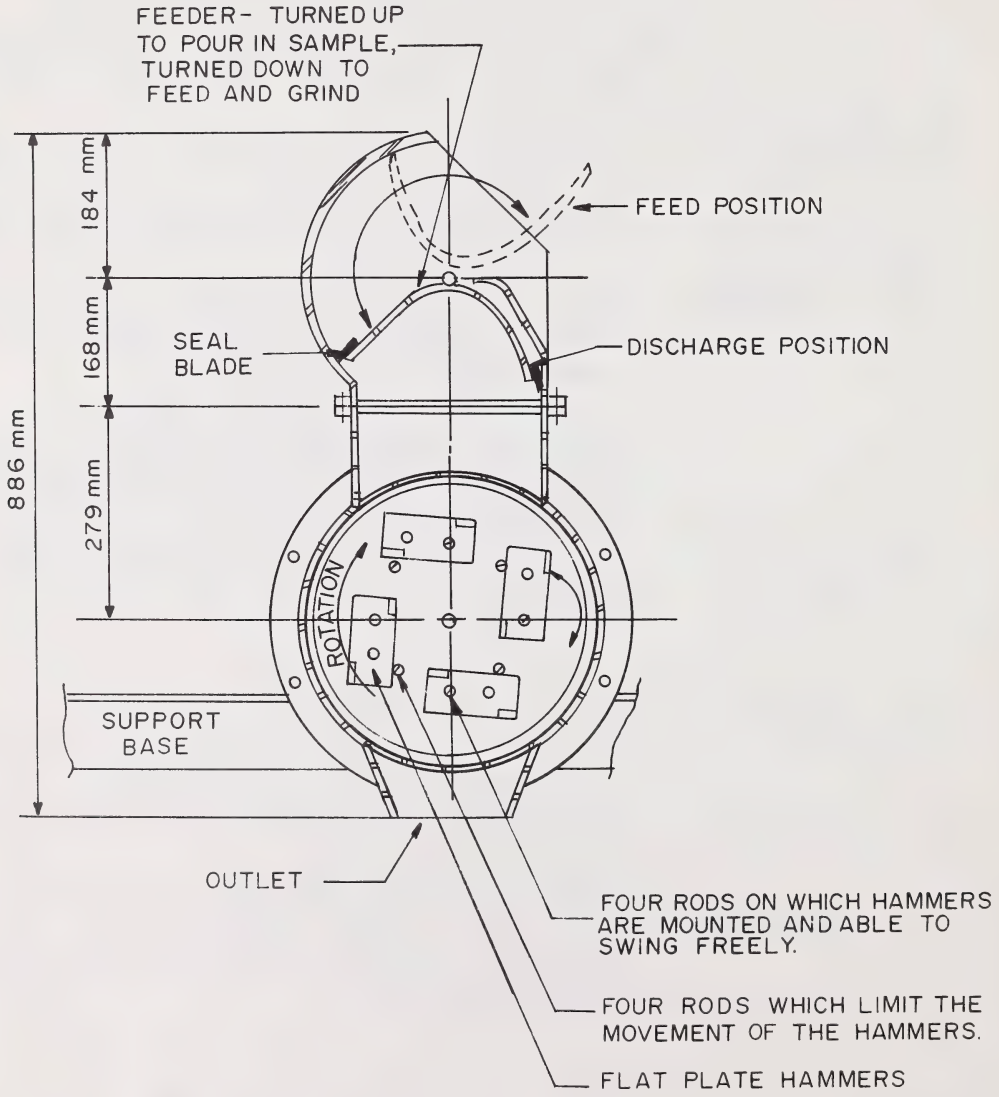


FIGURE 1 HAMMERMILL USED FOR REJECT SAMPLES

Preparation and Subsampling of Bulk Secondary Froth Samples

Scope: This method provides for the preparation and subsampling of bulk secondary froth samples.

Summary: Bulk secondary froth samples are initially acidified followed by thorough mixing on a wrist-action shaker. Adequate subsamples are removed before the bulk sample reverts to a discontinuous system.

Safety Considerations: Hydrochloric acid — highly toxic by inhalation. A strong irritant to eyes and skin.

Apparatus, Reagents, Materials:

1. Wrist-action shaker, type used for paint conditioning and capable of accepting 22.7 L containers.
2. Graduated cylinder — 25 mL.
3. Hydrochloric acid — A.C.S. reagent grade.
4. Pails with lids — 22.7 L.
5. Sample bottles — 125 mL.
6. Balance — 30 kg capacity, readability better than 0.1 kg

Procedure:

1. Bulk secondary froth samples, received in 22.7 L pails, should have a weight of approximately 7 kg. Weigh the sample and pail to the nearest 0.5 kg and subtract from this value the average weight of an empty 22.7 L pail. Transfer 1 mL concentrated HCl per 0.5 kg secondary froth to the sample and secure the lid.
2. Place the pail on the shaker and shake the acidified sample for 15 minutes.
3. Immediately (a) remove the container and tip it over a sump, allowing the contents to pour out gradually.
4. Slowly fill a 125 mL sample bottle ⅓ to ½ full by intersecting the stream with the lip of the bottle. Clean the outside of the sample bottle, and cap tightly.

Precision: Not applicable.

Comments:

a. The timing after the shaking of the acidified sample is critical to obtaining the best possible subsample. The subsample must be taken immediately following turn-off of the shaker.

Homogenization and Subsampling of Fluid Bulk Process Samples with an Automated Subsampler

Scope: This procedure describes the operation and use of an automated subsampling device for providing representative analytical-sized samples from bulk quantities of fluid material. Samples covered by the method include slurry, froth, middlings and tailings from the hot water extraction process, and feed, product, and tailings from froth treatment. The subsampler is limited to bulk samples within the volume range 1.8 to 2.0 L. However samples as small as 500 mL may be accommodated provided they are diluted to 2.0 L with a suitable solvent. The subsample size provided is adjustable from 10 to 50 mL per withdrawal.

Summary: A bulk sample is collected in or transferred to a sample pot and placed in position on the mixer platform of the subsampler. When the automatic sequence is initiated the pot is raised and seated within the subsampler head (Figures 1 and 2). The sample pot is then pressurized with nitrogen and a rotating impeller shaft is lowered into the sample (Figure 3). When the homogenization process is complete, a subsample of pre-selected size is withdrawn under pressure while the bulk sample is still in motion.

Background: The subsampler homogenizes a multiphase material using a combination of high shear dispersion by an impeller, turbulent mixing through a venturi-type draft tube, and high velocity recycle flow. A marine-type impeller rotates within the confines of a concentrically placed stationary draft tube. The impeller forces material outwards to the wall of the draft tube and upwards to the lid. The inside wall of the draft tube is contoured to induce further agitation of the flow and thus minimize inertial separation of the sample phases. On passing over the uppermost edge of the draft tube, the sample is pumped downwards into the annular space between the outer wall of the draft tube and the inner wall of the pot, once more to be forced through the impeller. The base of the pot and the head of the mixer are streamlined to avoid dead zones and promote the high flow recirculation pattern.

The unit is also equipped with a pneumatic subsample withdrawal system capable of sampling the bulk while in motion. This feature ensures that a representative subsample is obtained by eliminating bias that would be introduced under static sampling conditions due to solids settling and/or water coalescence.

In this design, the mixing chamber is also the container in which bulk samples may be collected. This eliminates transfer steps and consequent sample losses.

Safety Considerations: The automated subsampler is equipped with a number of interlock systems, regulators, and mechanical guards to ensure its safe operation. The following design features are of specific note:

i) Activation of the subsampler requires that two START buttons be pressed simultaneously. These buttons are located on the control panel away from moving parts and necessitate the use of both hands. Thus, fingers are prevented from being caught between the subsampler head and the rising sample pot.

ii) A time delay of approximately 5 seconds is provided between the start operation and impeller rotation. Should the sample pot not seat itself properly within the head, ample time is provided to terminate the automatic sequence.

iii) The STOP button located on the front of the control panel is a non-discretionary override switch, and hence serves as an emergency shutdown button. When depressed, all power and pressurization systems are immediately terminated.

iv) The sample pot and control panel housing are continually purged/pressurized with nitrogen to ensure safe operation with flammable materials.

Use of the automated subsampling device does not demand any unusual safety considerations beyond normal laboratory practice.

Apparatus, Reagents, Materials:

1. Automated subsampler — schematically illustrated in Figures 1 to 4. Features of the apparatus include:

   i) Air motor, 250 W, equipped with exhaust pressure variable speed control and tachometer.

   ii) Pneumatic cylinders to mechanize sample pot, impeller shaft, and sampling valve actions. Cylinders are connected to a series of electrical solenoids and solid state time delay relays integrated for automatic sequencing operations. With reference to Figure 1, the following descriptions are provided:

   Cylinder 1 29 mm dia. x 89 mm stroke, non-rotating
   Cylinder 2 29 mm dia. x 22 mm stroke, low profile
   Cylinder 3 29 mm dia. x 102 mm stroke

   Solenoid A 6.4 mm 2-way single solenoid valve
   Solenoid B 6.4 mm 4-way single solenoid valve
   Solenoid C 9.5 mm 2-way single solenoid valve
   Solenoid D 6.4 mm 4-way single solenoid valve
   Solenoid E 6.4 mm 4-way double solenoid valve

   Time Delays Relays TD1 variable 2-60 s
   TD2 variable 20-600 s
   TD3 variable 0.1-1 s
   TD4 variable 2-60 s

   iii) Marine type impeller — 76 mm dia.

   iv) Nitrogen pressurization system for subsample withdrawal regulated to 14 - 21 kPa(g) inside the pot.

   The subsampling device must be connected to a source of compressed air with a minimum pressure of 550 kPa(g) and a regulated nitrogen supply of 70-205 kPa(g) at source.

2. Supply of pre-cast aluminum sample pots with integral sampling port and piston assembly. Figure 4.

The following are required if bulk samples to be processed are less than 2 litres in volume:

3. Balance — 15 kg capacity, readable to 0.5 g.
4. Supply of dry 74% toluene/26% isopropyl alcohol (by volume), 1,1,1-trichloroethane, or toluene, depending on the solvent requirements for subsequent analysis.

Procedure:

Bulk Samples Collected Directly From Process Streams

1. With the sampling piston in the closed position (i.e. fully inserted), fill the sampling pot to within at least 10 mm of the rim. For froth streams, position the sample pot such that the sample enters the venturi and flows up the annular cavity between the draft tube and wall of the vessel. This will eliminate entrapped air pockets which would reduce the volume of sample collected. It is also recommended that several drops of concentrated HCl be added to froth samples to enhance emulsification during the mixing step.

Bulk Samples Requiring Transfer from Another Container

2. Weigh a clean sample pot to the nearest 0.5 g. Weigh the sample and container. Transfer the sample (500 mL minimum volume) to the pot using solvent which will not interfere with subsequent analysis as rinse. Dry and reweigh the original sample container. Add solvent to the contents of the sample pot to bring the level within 10 mm of the rim. Reweigh the sample pot.

   Clean the rim of the pot with a solvent-wetted cloth. Proceed to step 4.

Bulk Samples Requiring Dilution

3. Weigh a clean sample pot to the nearest 0.5 g. Place the sample (500 mL minimum volume) in the pot and reweigh. Add sufficient solvent to bring the contents of the pot within 10 mm of the rim and weigh again.

   Clean the rim of the pot with a solvent-wetted cloth. Proceed to step 4.

Operation of the Subsampler

4. Carefully place the filled sample pot on the mixer platform. Gently push the container to the back of the platform and rotate it counter-clockwise until the positioning pin on the sample pot locks against the retaining lip of the platform.
5. Open the manual valves on the compressed air and nitrogen supply lines and ensure adequate source pressures (550-690 kPa(g) for air and 70-205 kPa(g) for nitrogen). Turn the MASTER SWITCH key to the ON position and initiate the homogenization sequence by simultaneously depressing the two START buttons located on the side of the control panel.

   If for any reason it is necessary to terminate the automatic sequence, press the STOP button on the front of the control panel. This will immediately shut off all power and depressurize the system.

   The automatic operating sequence is:

   i) Solenoid E is powered, Cylinder 1 is extended and the sample pot platform is raised to seat itself within the subsampler head. Sampling piston locks into position.

   ii) Following a short delay provided by TD1 (adjustable, 3-5 s recommended), solenoids A,B, and C are powered to initiate the nitrogen pressurization, engage the air motor, and extend Cylinder 3 to drive the impeller into the bulk sample. TD2 is activated to provide a 120-300 s mixing period after which the SUBSAMPLE INDICATOR light goes on to indicate that samples may be withdrawn. During the homogenization period, circuitry to the SUBSAMPLE switch is open to prevent premature sample withdrawal.

   Adjust the air motor speed to 30-33 rev/s using the speed control valve located directly beneath the tachometer.

6. To obtain a subsample, position a small container underneath the spout of the sampling port on the pot and depress the SUBSAMPLE switch. This causes Cylinder 2 to retract and then quickly extend. The time that the sampling port remains open is governed by relay TD3. Subsample sizes typically obtained under 21 kPa(g) N_2 pressure at various time delay settings are shown below:

Time Delay (s)	Subsample Size (mL)
0.2	5-10
0.3	10-15
0.4	20-30
0.5	40
1.0	50

   A number of individual subsamples or a large subsample consisting of several increments may be taken by repetitively pressing the SUBSAMPLE switch.

Shutdown

7. Turn the subsampler off by depressing the STOP button. A shutdown sequence is initiated wherein the motor stops, the impeller is raised, and the pot is depressurized. Close the compressed air and nitrogen lines.

Cleanup

8. The sample pot and subsampler head/impeller assembly are most easily cleaned by emptying the contents of the pot, filling it with solvent, and re-activating the subsampler. Depressing the SUBSAMPLE switch several times will cleanse the sample port. When complete, dry the subsampler head and shaft with a cloth. Rinse the sample pot with a stream of high pressure water, invert, and allow to drain.

Calculations: Bulk Samples Requiring Transfer From Another Container

1. Calculate the weight fraction of sample in the subsample as:

$$\text{Weight Fraction of Sample} = \frac{\text{Wt. Sample and Container} - \text{Wt. Container}}{\text{Wt. Sample Pot and Contents} - \text{Wt. Pot}}$$

Bulk Samples Requiring Dilution

2. Calculate the weight fraction of sample in the subsample as:

$$\text{Weight Fraction of Sample} = \frac{\text{Wt. Pot and Sample} - \text{Wt. Pot}}{\text{Wt. Pot, Sample and Solvent} - \text{Wt. Pot}}$$

Precision: Not applicable.

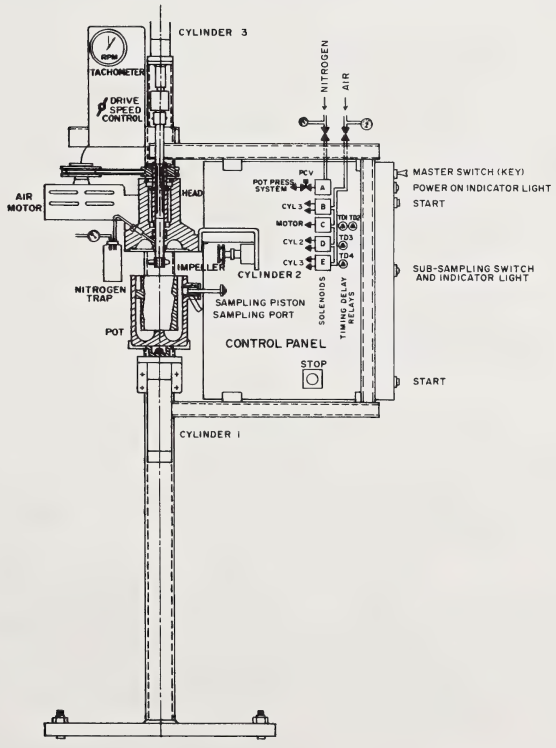


FIGURE 1: FRONT VIEW OF AUTOMATED SUBSAMPLER

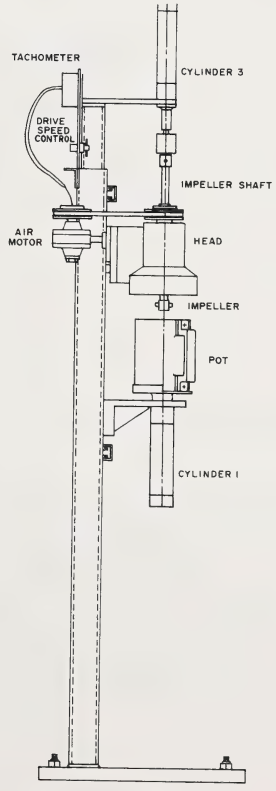


FIGURE 2: SIDE VIEW OF AUTOMATED SUBSAMPLER

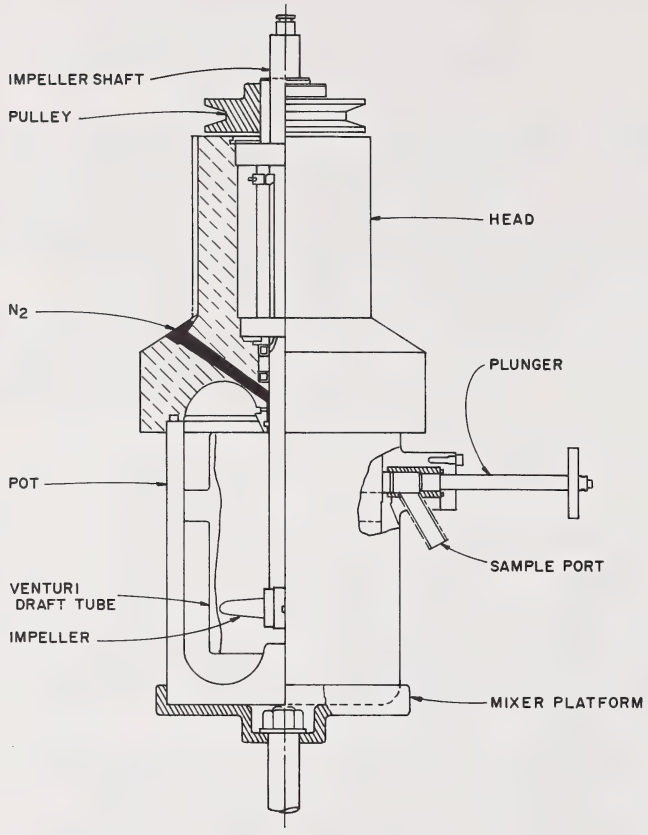


FIGURE 3: SUBSAMPLER HEAD

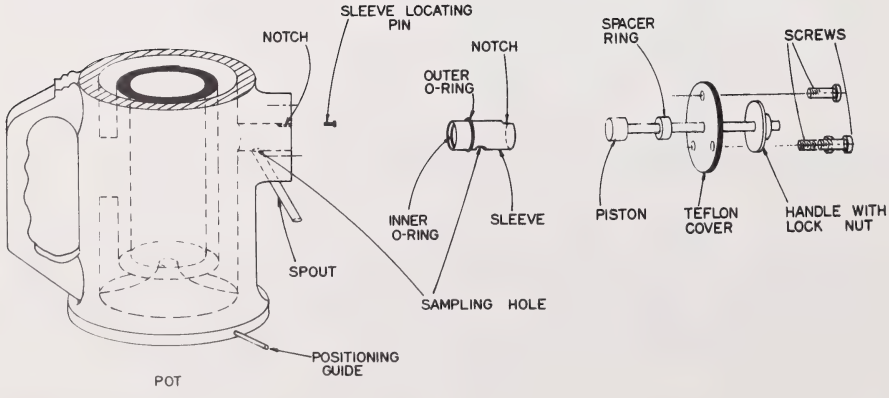


FIGURE 4: SAMPLE POT AND PISTON FOR THE AUTOMATED SUBSAMPLER

Aqueous Extraction of Oil Sand for Soluble Ion Content

Scope: This method describes the initial steps required for subsequent measurements of such soluble ions as Cl^-, CO_3^{-2}, HCO_3^-, SO_4^{-2}, K^+, Na^+, Mg^{+2}, and Ca^{+2} that are associated with oil sand.

Summary: Oil sand is mixed with boiling deionized water in such proportions as to simulate a slurry of 50 weight percent water. The aqueous portion of the slurry is clarified by centrifuging and filtration. Surface oil is removed from the clarified extract.

Background: This method is a crude simulation of the hot water extraction process. Its intent is to provide an estimation of the concentration of water soluble ions present in the aqueous portion resulting from the hot water extraction of oil sand. The concentration of these ions does not reflect a simple dilution of the aqueous phase of the oil sand. Since no direct correlation has been found between the amount of water added and the ion concentration, this method specifies a slurry of 50 weight percent water. In addition, caution must be exercised in interpreting the meaning of the resulting data.

The average water content of oil sand is assumed to be five weight percent.

Safety Considerations: No unusual safety considerations.

Apparatus, Reagents, Materials:

1. High speed centrifuge — 333 rev/s max., 39000 x G, 8 x 52 mL capacity, 8 place angle head.
2. Steel centrifuge tubes — 50 mL, with caps.
3. Boiling deionized water.
4. Beakers — 250 mL.
5. Graduated cylinder — 50 mL.
6. Spatula.
7. Polyethelyene bottles — 60 mL.
8. Disposable pipets.
9. Kimwipes — Type 900 S.
10. Top loading balance to ± 0.01 g, 1200 g capacity.

Procedure:

1. Weigh 50 ± 1 g oil sand into a 250 mL beaker. Add 45 mL boiling deionized water and mix thoroughly with a spatula until a smooth paste is formed. Allow the mixture to settle for 5 minutes.
2. Decant the aqueous phase of the mixture into a centrifuge tube. Balance the centrifuge tubes to 0.01 g using a disposable pipet and a top loading balance. Spin at 250 rev/s for 20 minutes. Decant the clarified water into a polyethylene bottle.
3. Remove any oil film present on the surface of the liquid by skimming with a folded Kimwipe. Cap the container tightly and store at cool temperatures, e.g. 4°C, until needed. The pH of the sample may be determined without further sample preparation. Ion analyses requires filtration of the sample through 0.45 μm filter paper as described in Method 1.8.

Calculations: Not applicable.

Precision: Not applicable.

Preparation of Process Water Samples for Ion Analysis

Scope: This method prepares the aqueous phase of process samples for subsequent analysis.

Summary: Any oily layer is removed and samples are centrifuged and filtered to remove any material larger than 0.45 μm. (1)

Safety Considerations: No unusual safety considerations.

Apparatus, Reagents, Materials:

1. Membrane filters — 3, 1.2, 0.8 and 0.45 μm, 47 mm diameter.
2. Holder for the above filters.
3. Vacuum filtering apparatus.
4. High speed centrifuge — 333 rev/s max., 39000 x G, 8 x 52 mL capacity, 8 place angle head.
5. Steel centrifuge tubes — 50 mL, with caps.
6. Glass jars with tops — 125 mL.
7. Disposable pipets.
8. Kimwipes — Type 900 S.
9. Top loading balance to ± 0.01 g, 1200 g capacity.

Procedure:

1. If the sample has an oily layer it is removed with a Kimwipe. If the sample appears cloudy, such as in the case of a middlings sample, it must be centrifuged prior to filtering. If a sample appears clear proceed to the filtration step.

Centrifuging

2. Fill a clean high speed centrifuge tube approximately ¾ full with sample. Do not shake the sample prior to pouring into the tube. Balance the tubes to 0.01 g using a disposable pipet and a top loading balance. Centrifuge the samples for 20 minutes at 250 rev/s. When the centrifuge has stopped, decant the liquid into a 125 mL jar and proceed with the filtration.

Filtration

3. Place a 0.45 μm membrane filter in its holder. Place the holder in a vacuum filtration set-up. Filter approximately 10 mL of sample (a). Disassemble the set-up and discard the filtered portion. Reassemble the set-up and filter the remaining sample. Decant the filtered sample into a 125 mL jar. The samples are now ready for analysis.

Calculations: Not applicable.

Precision: Not applicable.

Comments:

a. For some samples it will not be possible to filter through a 0.45 μm filter after centrifuging. In this case, start with a 3 μm filter, and proceed to 1.2 μm, 0.8 μm, and 0.45 μm filter.

Reference:

1. Analytical Methods Manual, Environment Canada, Inland Waters Directorate, Water Quality Branch, Ottawa, 1974.

CHAPTER 2

EXTRACTION PROCESS ANALYSIS

The most important and frequently-required analysis associated with the hot water extraction of oil sand is the determination of bitumen, water, and solids. The analysis of raw oil sand is required to evaluate reserves through core drilling programs and to monitor feed to lab scale batch experiments, pilot plants, or commercial scale plants. The analysis of process streams is needed to evaluate performance and provide data for mass balance calculations. It is therefore not surprising that the oil sand industry has given considerable attention to bitumen/water/solids determinations.

In 1955, a study comparing three laboratory methods for determining the bitumen content of oil sand was carried out (1). Briefly this revealed that a Soxhlet extraction using toluene as solvent and a Dean and Stark water trap was the best method. In this method hot toluene vapours pass through the oil sand and strip out water. The solvent and water vapour are condensed and report to the Dean and Stark trap. The water is retained in the graduated trap and the solvent is recycled through the sample where it dissolves the oil and carries it into the bulk of the solvent. The reflux is continued until the separation is complete. The solids are dried and determined gravimetrically, the water is determined by recording the volume in the trap, and the bitumen is determined by difference.

By 1973, Syncrude had modified the above procedure to include an improvement in the distribution of solvent, a correction for fines contained in the extract, the direct determination of the bitumen weight, and adaptation of the method to accommodate the widely varying compositions of different process streams. In that year, the Canadian Petroleum Association Tar Sand Council conducted a round robin study to compare the bitumen/water/ solids methods of several commercial and industrial laboratories (2). The study recommended the mass balance check provided by the direct bitumen determination and the correction for fines in the extract. The "classical" method as presented in this collection is applied to oil sand, slurry, and reject. In the case of froth, bitumen is determined by difference (Method 2.9). For middlings and tailings (Method 2.11) the modification includes the use of a larger extraction apparatus to accommodate a 250 to 600 g sample, the determination of bitumen from a density measurement on the extract, and the determination of water by difference. The use of density for the determination of bitumen replaces a spectrophotometric method which had previously been used for middlings and tailings. The spectrophotometric bitumen determination was based on the infrared absorbance at 2924 cm^{-1} and required the use of benzene as solvent. On the other hand, the use of density for the bitumen determination permits the substitution of toluene for the highly toxic benzene.

These classical methods based on prolonged reflux require 12 to 24 hours to complete the analysis. Frequently, a much faster turnaround time is desired. Consequently studies were undertaken to develop faster methods. Criteria for a new bitumen/water/solids analysis were:

- an analysis time of less than one hour
- accuracy and precision equivalent to the classical methods
- safety
- utilization of simple techniques and equipment.

The method for oil sand which we have developed is based on the cold extraction of bitumen and water into a dry solvent blend of 74% toluene and 26% isopropyl alcohol by volume. The toluene is present to extract bitumen while the isopropyl alcohol dissolves water. The extraction of oil sand with this solvent results in a two phase system. The solvent blend, bitumen, and water form one phase while the solids constitute the other.

After the coarse solids are allowed to settle, a portion of the extract is filtered through a 0.45 μm filter. An aliquot of the filtered mixture is applied evenly to cover a preweighed glass fiber filter. After evaporation of the solvent and water, the bitumen remaining on the filter is weighed. The gravimetric technique for bitumen is employed since the only universal parameter for bitumen determination is mass.

An aliquot of the unfiltered extract is analyzed by Karl Fischer titration to determine the water content of the sample. The Karl Fischer determination is fast and simple and is preferred over other techniques such as gas chromatography.

The solids may be determined by difference, however they are normally filtered and weighed to serve as a mass balance check.

Different sample streams require slight modifications to this basic oil sands method. For example, reject samples require a longer extraction time and a centrifuging step to separate the coarse solids before proceeding

with the bitumen and water determination.

Although a larger amount of the solvent blend is used for froth analysis, some samples have water contents that exceed its water dissolution capacity. Rather than increasing the quantity of solvent blend, Method 2.9 adds dry isopropyl alcohol if required to dissolve all the water.

The calculations for each method are presented with the procedures. These calculations take account of the volume change in the solvent blend due to the dissolution of water and bitumen.

The large amount of water and low bitumen content of middlings and tailings streams require a more dramatic alteration of the above methods. For these sample streams 1,1,1-trichloroethane was selected as solvent for the extraction. This solvent dissolves only the bitumen. The bitumen/1,1,1-trichloroethane phase is separated from the water and solids using phase separating paper. Again the bitumen is determined gravimetrically by dispersing an aliquot of the extract on a glass fiber filter and allowing the solvent to evaporate. The solids are dried and weighed and the water is determined by difference.

In this collection, the new bitumen/water/solids methods are denoted as "Syncrude" methods to distinguish them from the classical methods. The Syncrude designation also indicates that these methods are now the standard laboratory practice at Syncrude Research.

References

1. Draper, R.G., Yates, A. and Chantler, H. McD. "A Comparison of Three Laboratory Methods for Determining the Bitumen Content of Bituminous Sands." Canada Department of Mines and Technical Surveys, Mines Branch, Report No. FRL-211 of the Fuels Division, 1955.
2. The Canadian Petroleum Association Tar Sands Council. "Round Robin Study of Analytical Procedures of Various Laboratories on Assay Analysis of Athabasca Tar Sands." 1974.

Lab Scale Hot Water Extraction of Oil Sand

Scope: A laboratory batch extraction unit provides a useful aid for approximating the hot water extraction process. In conjunction with appropriate bitumen/water/solids analyses, the effect of operating parameters, feed variability and chemical additives on the processability of oil sand may be evaluated. Details outlining operation of the unit and subsequent derivation of oil recoveries are presented in this procedure.

Summary: Oil sand and water are slurried in the stainless steel pot of the batch extraction unit and the mixture is aerated. A predetermined amount of flood water is introduced and the floated primary froth retrieved. Further mixing and aeration allows the recovery of secondary froth. Samples of oil sand feed and the recovered froths are submitted for bitumen/water/solids analysis, thus allowing oil recoveries to be calculated on an input basis.

Safety Considerations: No unusual safety considerations.

Background: The design, operation, and an illustrative application of this laboratory batch extraction unit have been documented elsewhere (1,2).

Apparatus, Reagents, Materials:

1. Batch extraction unit and related components. The assembly is described in Figures 1 to 4.
2. Constant temperature water bath maintained at 82°C. A pump allows water to be circulated from the bath to a jacket surrounding the stainless steel pot.
3. Timing device.
4. Hot plate.
5. Sample bottles — 125 mL.
6. Beaker — 2 L.
7. Distilled water.

Procedure:

1. Ensure all air and water connections are sealed. Allow water from the bath to circulate through the surrounding jacket of the unit.
2. Heat approximately 1500 mL distilled water to 90°C on a hot plate. Homogenize a quantity of the oil sand under test and submit three representative samples for bitumen/water/solids analysis. Collect 500 g of the remaining sample and weigh to the nearest 0.1 g.
3. Transfer 150 mL of the hot water to the stainless steel pot. Lower the motor and impeller assembly to its lowest possible position on the shaft rod (impeller — 6 mm from the bottom) and turn on. Allow the remaining water on the hot plate to cool to 82°C.
4. Add the 500 g oil sand sample to the pot. Within as little time as possible:
   - Raise and lower the motor assembly to break up oil sand lumps present and leave the impeller 20 mm above the bottom of the vessel.
   - Adjust mixer to 10 rev/s.
   - Turn on air flow and adjust to approximately 7.0 mL/s on the flowmeter.
   - Start timer.

   Mix in this manner for 10 minutes.
5. When complete, turn the air supply off and flood the mixture with approximately 1000 mL of 82°C water, thus bringing the froth level to the top of the pot. Mix for an additional 10 minutes at 10 rev/s (no air).
6. Cease mixing and skim as much primary froth as possible from the top of the pot with the specially designed spatula. Collect the froth in a 125 mL sample bottle and submit for bitumen/water/solids analysis.

7. For recovery of secondary froth mix the remaining material for 5 minutes at 13 rev/s while aerating at approximately 3.9 mL/s. Collect secondary froth in the same manner as the primary froth and submit for bitumen/water/solids analysis.
8. Drain the residual material from the bottom valve and wash the pot and impeller with toluene. When shut down, ensure that the circulating water pump and air flow are turned off.

Calculations: When results for the bitumen, water and solids content of samples submitted have been obtained, calculate oil recoveries in the following manner.

Calculate the total weight of bitumen input to the system by initially averaging the percent oil value for the 3 oil sand samples submitted and multiplying this value by the weight of oil sand added to the stainless steel pot.

Recoveries are found as follows:

$$\text{Primary Recovery \%} = \frac{\text{Wt. Bitumen in Primary Froth (g)}}{\text{Wt. Total Bitumen (g)}} \times 100$$

$$\text{Secondary Recovery \%} = \frac{\text{Wt. Bitumen in Secondary Froth (g)}}{\text{Wt. Total Bitumen (g)}} \times 100$$

Total Recovery % = Primary Recovery + Secondary Recovery

Discrepancies from 100% Total Recovery are attributed to oil losses in the tailings, middlings, and that retained by the walls and impeller of the stainless steel pot (a).

Precision: Given an experienced operator, a homogeneous supply of oil sand prepared in accordance with Method 1.2, and strict adherence to the procedure as outlined, the precision of replicate bitumen recovery determinations is typically $\pm 2\%$ of the mean value. More specific statements regarding the reliability of recovery values are precluded due to the diversities of feed material, chemical additives, and operational conditions which may be employed for evaluating oil sand processibility.

Comments:

a. Residual material held in the stainless steel pot after recovery of the secondary froth may be differentiated as either secondary tailings or primary tailings in the following manner.
   - Allow the mixture to settle one minute from the time mixing and aeration ceases.
   - Decant the aqueous phase and denote as secondary tailings.
   - The remaining heavier particles are termed primary tailings.
   - Oil losses to the primary and secondary tailings may be obtained from bitumen/water/solids analyses of the samples.

References:

1. Sanford E.C. and Seyer F.A. American Chemical Society Division of Fuel Chemistry Preprint 23 (4), 54-62 (1978).
2. Sanford E.C. and Seyer F.A. CIM Bulletin 72 (803), 164-169 (1979).

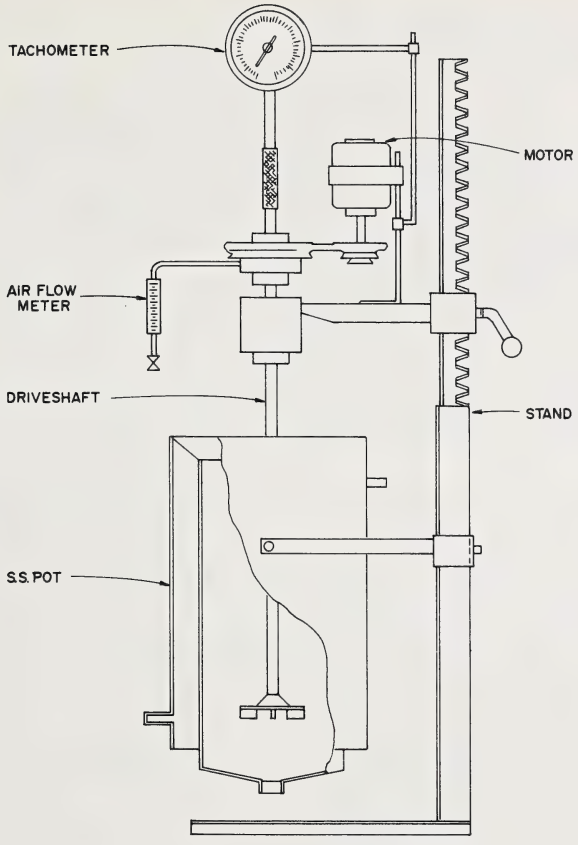


FIGURE 1: BATCH EXTRACTION UNIT

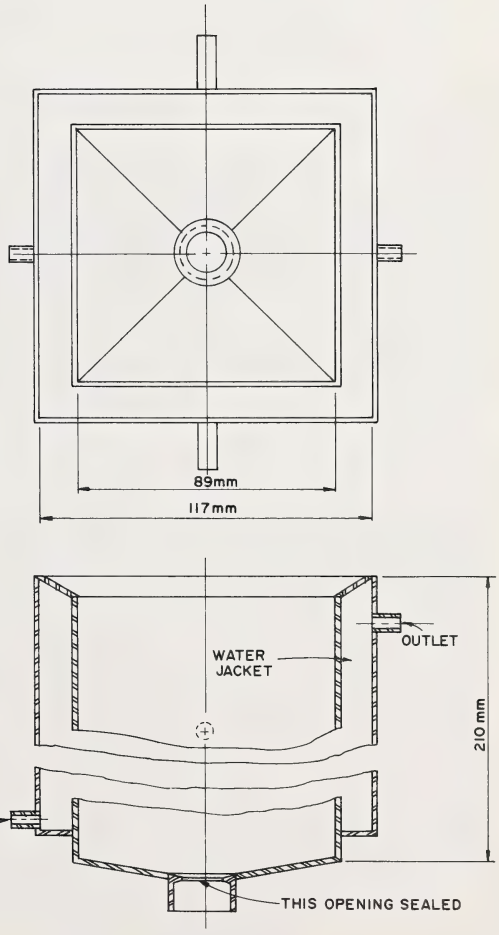
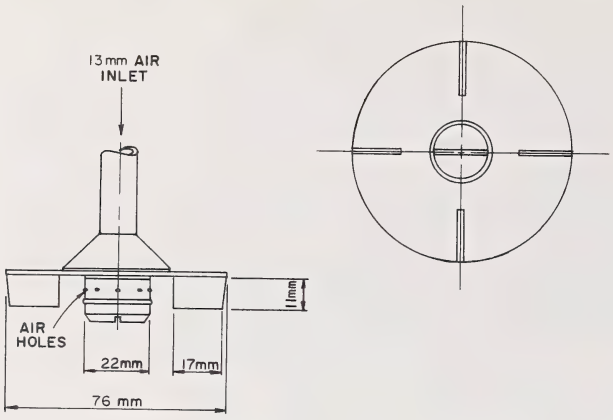
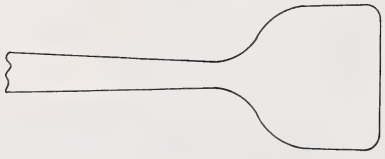


FIGURE 2: STAINLESS STEEL POT



IMPELLER



FROTH RETRIEVAL SPATULA

FIGURE 3: IMPELLER AND FROTH RETRIEVAL SPATULA

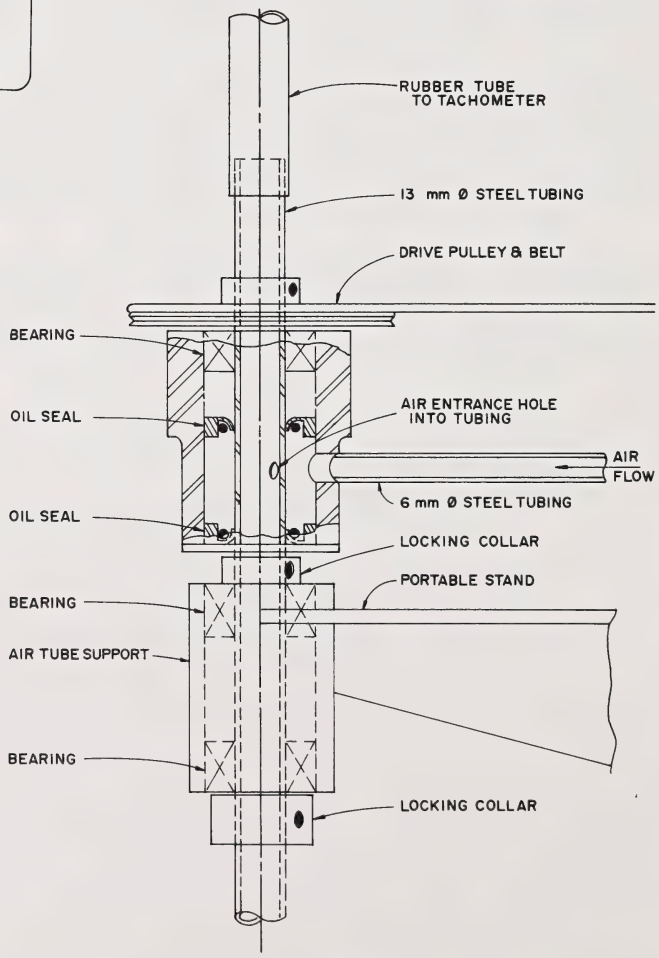


FIGURE 4: IMPELLER SHAFT AND AIR INTRODUCTION SYSTEM

Determination of pH of Aqueous Oil Sand Extracts

Scope: This method determines the pH of water derived from the hot water extraction of oil sand by Method 1.7.

Summary: A combination pH electrode and pH meter are used to determine the pH of water derived from oil sand.

Background: The measurement of pH is a common laboratory procedure. The application of this determination to aqueous samples derived from oil sand encounters two problems. First, the removal of oil from the sample may be incomplete. Fouling of the electrode with oil yields sluggish electrode response and tends to bias results towards high pH. The oil contamination may be removed through rinsing the electrode with toluene and acetone, followed by thorough rinsing with distilled water. Secondly, the pH measurement may be sluggish even after oil has been eliminated from the sample. This slow achievement of equilibrium may be alleviated through the use of a calomel reference combination pH electrode (1).

Safety Considerations: No unusual safety considerations.

Apparatus, Reagents, Materials:

1. A pH meter readable to two decimal places or better.
2. Combination pH electrode.
3. Buffer solutions — pH 7.00 and 9.00 at 25°C.
4. Supply of 15 mL beakers.

Procedure:

1. The electrode and pH meter are calibrated using the buffer solutions in accordance with manufacturer's instructions. If room temperature differs from 25°C, the pH of the buffer at room temperature is determined from the data provided by the supplier of the buffers used in the calibration. The electrode is rinsed copiously with distilled water and blotted dry between measurements.
2. Decant the sample into a 15 mL beaker. Place the electrode into the sample and record the pH when the meter has stabilized to the nearest 0.01 pH units. Readings are considered stabilized when there is no fluctuation in the second decimal place over a period of 15 to 20 s.

Calculations: Not applicable.

Precision: Strict precision evaluations on pH measurements as they relate to aqueous samples obtained from oil sands have not been undertaken. Replicate determinations are, however, generally considered repeatable to 0.1 pH unit. Precision associated with the actual pH measurement is likely to be much better than the uncertainties involved in preparing the aqueous sample from oil sand.

Reference:

1. Hach Chemical Company. News and Notes for the Analyst. Vol. 1, No. 2 (1976).

Determination of Metal Content in Aqueous Samples by Inductively Coupled Argon Plasma Emission Spectroscopy

Scope: This method determines the content of various metals in aqueous samples. The elements analyzed are: Al, Ag, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, Zn, Zr. A list of detection limits and maximum concentrations is provided in Table 1. Samples with higher concentrations can be accommodated by dilution.

Summary: Samples prepared by Method 1.8 are aspirated into the plasma of an inductively coupled argon plasma emission spectrometer (I.C.A.P.). The emission intensity of each element is measured and compared with those of standards to arrive at a sample concentration in mg/L.

Background: Flame emission spectroscopy has been used for many years for the determination of a number of metals in aqueous samples. The conventional flame emission technique however suffers from limitations due to the useful concentration ranges, compound vaporization temperature, and serious interelement interferences.

The I.C.A.P. technique provides major advantages over the conventional flame. The high temperature (10 000°K) results in complete vaporization of essentially all compounds. The argon gas atmosphere and high electron density of the plasma eliminates virtually all chemical interferences. Emission interferences due to the close proximity of lines of other elements to a measured line are corrected automatically, provided that they are included in the program set into the instrument's computer. Some matrix effects associated with the nebulizer operation remain, mostly due to surface tension changes affecting nebulizer efficiency. The I.C.A.P. technique exhibits an exceptional range of linear response, as shown in Table 1. It also provides analysis for all fitted elements in about the same time needed to measure one element by atomic absorption.

Safety Considerations:

1. I.C.A.P. — avoid direct exposure to the high intensity ultraviolet light produced by the plasma. Appropriate precautions are required in dealing with the very high voltages in the plasma generator.
2. Hydrochloric acid — highly toxic by inhalation. A strong irritant to the eyes and skin.
3. Nitric acid — extremely corrosive. A powerful oxidizing agent.

Apparatus, Reagents, Materials:

1. Inductively coupled argon plasma spectrometer — Jarrell-Ash Model 96-986 with 96-978 "N + 1" channel and detectors for the elements listed in Table 2. Jarrell-Ash Division, Fisher Scientific Co., 590 Lincoln Street, Waltham, MA 02154.
2. Pump (a) — Gilson Minipuls model MP1 with 0.63 mm ID polyvinyl chloride manifold tubing. Gilson Medical Electronics Inc., P.O. Box 27, 3000 West Beltline Highway, Middleton, WI 53562.
3. 1 mL micropipet — Oxford P-7000 sampler with tips.
4. Volumetric flasks — 100 mL, Class A.
5. Nalgene linear polyethylene bottles — 125 mL, with polypropylene screw closures. Nalge 2104.
6. Nitric acid — A.C.S. reagent grade.
7. Hydrochloric acid — A.C.S. reagent grade.
8. 100 mg/L stock solution of Ag.
9. 1000 mg/L stock solutions of Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Sn, Si, Ti, V, Zn, Zr.
10. Deionized water.
11. 1000 mg/L Yttrium solution.

Procedure: Standard Preparation

1. The standards are identified by the names AQU1 to AQU5. They are prepared as follows:

Standards	Preparation
AQU1	To a 100 mL volumetric flask add 1 mL HNO_3 and 1.0 mL of 100 mg/L Ag.
AQU2	To a 100 mL volumetric flask add 1 mL HNO_3 and 1.0 mL each of the following: 1000 mg/L stock solutions of Cu, Cr, Ni, V.
AQU3	To a 100 mL volumetric flask add 3 mL of HCl and 1.0 mL each of the following: 1000 mg/L stock solutions of Ca, Cd, Co, Mg, Mn, Pb, Zn, Zr.
AQU4	To a 100 mL volumetric flask add 5 mL of HCl and 1.0 mL each of the following: 1000 mg/L stock solutions of Al, Ba, Fe, Sn, Ti.
AQU5	To a 100 mL volumetric flask add 1.0 mL of the following: 1000 mg/L stock solutions of B, K, Mo, Na, P, Si.

Dilute all standards to volume with distilled water and shake. Store the standards in 125 mL Nalgene bottles.

Sample Preparation

2. Samples are prepared by Method 1.8.

Analysis of Samples and Standards

3. Call up matrix WTR5 (b). A copy of matrix is shown in Figure 1.
4. Set up the instrument for the specific nebulizer in use (c). Typical conditions are:

Power	1.15 kW
Observation height	17 mm above coil
Nebulizer Pressure	140 kPa(g)
Coolant Gas	330 mL/s argon
Plasma Gas	33 mL/s argon to light
	17 mL/s argon to operate
Sample Gas	No flow to light
	10 mL/s argon to operate
Sample Uptake (a)	13 μL/s

When properly adjusted, the red emission tip produced by a 1000 mg/L Yttrium solution should be 10 mm below the entrance slit of the main monochromator.

5. Set the N + 1 monochromator for the 769.8 nm K line. Confirm the setting with a K solution. The slit of the N + 1 should be set 15 mm above the plasma work coil. Slit width should be 50 μm. The dynode resistor switch should be set at 7.
6. Aspirate each of the standards using 3 burns each, with an EGGGN command. Standardize, then check the AQU3 standard for correct analysis (10.0 mg/L of each element).
7. Analyze each sample. Check the AQU3 standard after each 5 samples.

Calculations: The computer of the I.C.A.P. system prints out the analysis result directly in mg/L.

Precision: The precision of the I.C.A.P. analysis for metals in aqueous samples is directly proportional to the concentration of elements present. Within a range from ten times the detection limit to the maximum concentration programmed into the system, the relative standard deviation among results from replicate burns is typically ± 1% of the mean concentration.

Comments:

a. While use of the pump to control sample flow rate to the nebulizer is not essential, it greatly reduces operating problems caused by minor variations in nebulizer performance.

b. The matrix is the program which sets up the set of elements to be measured, interelement corrections, and measurement time on the Jarrell-Ash system. The matrix WTR5 shown in Figure 1 is a currently used version at Syncrude Research. However, interelement corrections and upper concentration limits will change depending upon nebulizer and hardware performance.

c. Each nebulizer, as currently available for I.C.A.P., requires slightly different operating conditions. It is recommended that the instrument data, nebulizer information supplied by the manufacturer, and information obtained by experience with each nebulizer be assembled into an "I.C.A.P. Data Book" for easy reference. The data book must be kept current by noting instrument changes and data on new nebulizers.

Table 1.
DETECTION LIMITS AND MAXIMUM CONCENTRATION FOR WTR5

Element	Detection Limit (mg/L)	Maximum Concentration (mg/L)
Al	0.0229	700.0
Ag	0.0039	100.0
B	0.0053	1000.0
Ba	0.0012	500.0
Ca	0.0068	1000.0
Cd	0.0166	100.0
Co	0.0045	500.0
Cr	0.0040	500.0
Cu	0.0028	500.0
Fe	0.0036	1000.0
K	0.0200	5000.0
Mg	0.0332	1000.0
Mn	0.0010	100.0
Mo	0.0508	1000.0
Na	0.0094	3500.0
Ni	0.0408	500.0
P	0.0616	1000.0
Pb	0.0338	100.0
Si	0.0164	340.0
Sn	0.0352	1000.0
Ti	0.0014	200.0
V	0.0037	300.0
Zn	0.0045	100.0
Zr	0.0045	500.0

Table 2.
ATOMIC EMISSION SPECTROMETER

Wavelength (nm)	Physical Channel	Element	Photo-Multiplier Tube	Resistor (Ω)	Capacitor (μF)
203.844	1	Mo	427C	2.2M	0.001
213.856	50	Zn	427B	1.0M	0.01
214.914(x2)*	19	P	427B	1.0M	0.001
220.351	2	Pb	427C	2.2M	0.001
226.502	3	Cd	427C	2.2M	0.01
238.892	49	Co	300D	1.0M	0.01
249.7(x2)	25	B	427B	3.3M	0.01
251.6	48	Si	300D	3.3M	0.01
257.610	4	Mn	300E	1.0M	0.01
259.940	5	Fe	300E	1.5M	0.01
267.716	6	Cr	300D	1.5M	0.01
279.079	7	Mg	300D	220K	0.1
283.989	9	Sn	300D	200K	0.01
292.402	10	V	300D	2.7M	0.01
308.215	11	Al	300D	2.2M	0.01
317.933	12	Ca	300E	1.0M	0.01
324.754	14	Cu	300E	4.7M	0.01
328.068	15	Ag	300D	2.2M	0.01
334.941	16	Ti	300E	4.7M	0.01
339.198	17	Zr	300E	2.2M	0.01
341.476	18	Ni	300E	1.5M	0.01
435.8	13	Hg	300E	10.0M	0.1
493.409	24	Ba	300E	1.0M	0.1
588.995	22	Na	300C	2.2M	0.01
	47	N + 1	456HA	Var	0.02
	26	Int.Std.	—	—	—
	20	Int.Std.	—	—	—

* Second Order

```
 PR
MX NAME:WTR5
MX NAME:WT
# OF LCN'S:24  # OF SM'S:  1
MODE:CN
FORMAT:  1 1Ø 1Ø  4
IS# 1    PCN:26 PRTY: 1 PREBRN: 1 EXPOSR: 1Ø
IS# 2
IS# 3
IS# 4
STD# 1 AQU1
STD# 2 AQU2
STD# 3 AQU3
STD# 4 AQU4
STD# 5 AQU5

 1 ZR 17  1  Ø  3  1  4  1 ABCD     Ø 1Ø.ØØ     Ø 2.Ø11 -.283
 2 CR  6  1  Ø  2  1  4  1 ABCD     Ø 1Ø.ØØ     Ø 4.3Ø1 -.4Ø3
 3 NI 18  1  Ø  2  1  4  1 ABCD     Ø 1Ø.34     Ø 2.951 -2.Ø3
 4 CU 14  1  Ø  2  1  4  1 ABCD     Ø 1Ø.23     Ø 1.221 -.159
 5 FE  5  1  Ø  4  1  4  1 FEWA     Ø 1Ø.ØØ     Ø 1.881 -.263
 6 CD  3  1  Ø  3  1  4  1 ABCF     Ø 1Ø.12     Ø 1.113 -2.Ø6
 7 CO 49  1  Ø  3  1  4  1 ABCD     Ø 1Ø.ØØ     Ø 2.549 -.252
 8  P 19  1  Ø  5  1  4  1 ABCE     Ø 1Ø.Ø6     Ø 24.12 -1.61
 9 AL 11  1  Ø  4  1  4  1 ALWA     Ø 1Ø.ØØ     Ø 2.691 -1.6Ø
1Ø SI 48  1  Ø  5  1  4  1 ABCG     Ø 1Ø.1Ø     Ø 6.13Ø -.385
11 ZN 5Ø  1  Ø  3  1  4  1 ABCF     Ø 1Ø.ØØ     Ø 1.716 -.Ø73
12 MO  1  1  Ø  5  1  4  1 ABCE     Ø 1Ø.ØØ     Ø 1.927 -.649
13 MG  7  1  Ø  3  1  4  1 ABCE     Ø 1Ø.ØØ     Ø 2.749 -1.77
14  V 1Ø  1  Ø  2  1  4  1 VVWA     Ø 1Ø.ØØ     Ø 1.929 -.35Ø
15 MN  4  1  Ø  3  1  4  1 ABCF     Ø 1Ø.ØØ     Ø 1.8Ø8 -.Ø65
16 TI 16  1  Ø  4  1  4  1 TIWA     Ø 1Ø.ØØ     Ø 1.885 -.124
17 AG 15  1  Ø  1  2  4  1 ABDF     Ø 1Ø.ØØ     Ø .7576 -.284
18 B  25  1  Ø  5  1  4  1 ABCE     Ø 1Ø.ØØ     Ø 19.96 -.747
19 BA 24  1  Ø  4  1  4  1 ABCD     Ø 1Ø.ØØ     Ø 3.166 -.Ø65
2Ø CA 12  1  Ø  3  1  4  1 CAWA     Ø 1Ø.Ø1     Ø 3.825 -.7Ø6
21 NA 22  1  Ø  5  1  4  1 NAWA     Ø 26.36     Ø 4.952 -.247
22 PB  2  1  Ø  3  1  4  1 ABCF     Ø 1Ø.Ø3     Ø 3.45Ø -1.69
23 SN  9  1  Ø  4  1  4  1 SNWA     Ø 1Ø.ØØ     Ø 4.487 -1.99
24 N+ 47  1  Ø  5  1  4  1 NIWA     Ø 1Ø.ØØ     Ø 24.58 - 3.52

48 1Ø .ØØ34
18 1Ø .ØØ56
11 1Ø .ØØ35
12 1Ø .ØØ12
 3 1Ø .ØØ22
 5 1Ø .ØØ13
```

FIGURE 1 PRINTOUT OF MATRIX WRT5

1	1Ø	.ØØØ9
19	1Ø	.ØØ19
9	1Ø	.ØØ42
47	1Ø	.ØØ26
18	17	.12Ø5
11	17	.ØØ14
12	17	.ØØ14
3	17	.ØØ44
6	17	.ØØ12
7	17	.ØØ13
19	17	.ØØ17
9	17	.ØØ49
47	17	.ØØ61
3	18	.Ø58Ø
14	18	.Ø234
2	18	.ØØ22
5Ø	18	.ØØ3Ø
1	11	.ØØ11
2	11	.ØØ11
15	17	.ØØ37
19	18	.ØØ24
19	3	.ØØ19
18	49	.Ø147
3	49	.ØØ79
25	49	.ØØ22
1	49	.ØØ33
2	49	.ØØ29
5	6	.ØØ97
47	6	.ØØ29
9	6	.2Ø15
18	14	.Ø289
3	14	.ØØ23
19	14	.ØØ75
2	14	.ØØ14
5Ø	14	.ØØ42
3	5	.Ø128
49	5	.Ø132
19	5	.ØØ18
9	5	.ØØ16
19	7	.ØØ17
9	7	.ØØ34
11	4	.ØØ14
19	4	.ØØØ9
9	4	.ØØ13
7	4	.ØØ18

FIGURE 1 (continued)

```
1Ø  1 .ØØØ9
17  1 .ØØØ9
18  1 .ØØØ7
11  1 .ØØ5Ø
12  1 .ØØØ8
 3  1 .ØØ23
 7  1 .ØØØ8
48  1 .ØØ54
19  1 .ØØ44
 2  1 .ØØ21
 9  1 .ØØ19
19 48 .ØØ18
1Ø 16 .ØØ13
 3 48 .ØØ17
17 16 .ØØ24
18 16 .ØØ61
12 16 .ØØ2Ø
 3 16 .ØØ78
47 16 .ØØ15
19 5Ø .ØØ17
48 5Ø .ØØØ9
48 19 .ØØ24

CURVE NAME :VVWA
3ØØ.ØØØ 3ØØ.ØØØ
      Ø       Ø
CURVE NAME :ABCD
5ØØ.ØØØ 5ØØ.ØØØ
      Ø       Ø
CURVE NAME :ALWA
7ØØ.ØØØ 7ØØ.ØØØ
      Ø       Ø
CURVE NAME :ABCE
1ØØØ.ØØ 1ØØØ.ØØ
      Ø       Ø
CURVE NAME :CAWA
1ØØØ.ØØ 1ØØØ.ØØ
      Ø       Ø
CURVE NAME :FEWA
1ØØØ.ØØ 1ØØØ.ØØ
      Ø       Ø
CURVE NAME :NAWA
35ØØ.ØØ 35ØØ.ØØ
      Ø       Ø
```

FIGURE 1 (continued)

Determination of Chloride in Aqueous Samples by Constant Current Coulometry

Scope: This method determines the chloride concentration of aqueous samples containing more than 5 mg/L chloride.

Summary: An aliquot of the sample is introduced into a vial containing a buffer reagent of nitric acid, acetic acid and polyvinyl alcohol. A silver anode generates the titrant Ag^+ ions, which precipitate the Cl^- ions. The end point is determined by an electrode pair that sensitively monitor the concentration of Ag^+ ion. When excess Ag^+ ion is detected generation of the titrant is terminated. The Cl^- ion concentration, which is based on the current required to generate the Ag^+ ion, is read directly in mg/L.

Background: The concentration of chloride ions in oil sand water (Method 1.7) is highly variable. As a result chloride analysis is of interest to study this variability and the effect it may impose upon the hot water extraction process.

The method described here and the Mohr titration have been applied to chloride determinations. Both methods involve the precipitation of chloride with silver ions. The present method is somewhat less accurate than manual titrations but provides some significant advantages. In studying oil sand water and aqueous process streams it is time-consuming to produce the larger volumes of cleaned water required for the manual titration. It is also frequently impossible to obtain a colourless sample and the resultant colorimetric end points are very difficult to detect. The small sample size and the amperometric end point determination of the Buchler Chloridometer used in this procedure resolve both these problems.

The Buchler instrument readout is given directly in milliequivalents of chloride per liter for a sample of 0.01 mL. The great majority of analyses are desired in mg/L. Since there are 35.4 mg per milliequivalent for chloride, the reading can be made direct in mg/L by increasing the volume by 35.4, i.e. by titrating 0.354 mL of sample. For higher concentrations, samples of 0.0354 mL may be titrated and the appropriate tenfold correction applied to the readout.

The method described here is general in nature. Three sample preparation comments are noteworthy for applying the method to particular process streams. First, aqueous samples with a high dissolved organic content can be analyzed directly, but the electrodes must be cleaned after each measurement. Secondly, caustic solutions containing more than 20 wt % NaOH must first be neutralized with glacial acetic acid. Finally, extraction process streams such as middlings must be centrifuged and filtered as described in Method 1.8.

Interferences: This method, like all silver precipitation techniques, measures all components which form insoluble silver compounds. Thus it measures the total milliequivalents of chloride, bromide, iodide, and sulfide among the common anions. Since chloride usually is present in far greater amounts than the others during oil sand processing, the result is normally considered to be chloride only.

Safety Considerations:

1. Nitric acid — extremely corrosive. A powerful oxidizing agent.
2. Acetic acid — a skin and eye irritant. Flammable.
3. Caution should be exercised when mixing nitric and acetic acid solutions.

Apparatus, Reagents, Materials:

1. Chloridometer — Buchler Model 4-5000. Buchler Instruments Division, Nuclear Chicago, 1327 Sixteenth St., Fort Lee, NJ 07024.
2. Two pipets — Gilson Pipetman adjustable with tips. Gilson Medical Electronics Inc., P.O. Box 27, 3000 West Beltline Highway, Middletown, WI 53562.
3. Auto-dispenser — 3 mL.

4. Volumetric flasks — 100 and 1000 mL, Class A.
5. Silver polish.
6. Measuring pipet — 10 mL.
7. Beaker — 500 mL.
8. Distilled or deionized water free of chlorine or chloride ions.
9. Reagents:
   Glacial acetic acid, A.C.S. reagent grade
   Nitric acid, A.C.S. reagent grade
   Polyvinyl alcohol.

Procedure:

1. Adjust the pipets to deliver 0.354 mL and 0.0354 mL.

Preparation of Buffer Reagent

2. Place 1.8 g of powdered polyvinyl alcohol and 100 mL of distilled water in a beaker. Heat just to boiling and stir the solution until all the polyvinyl alcohol dissolves. Allow the polyvinyl alcohol solution to cool to room temperature.
3. Add 6.4 mL of concentrated nitric acid and 100 mL of glacial acetic acid to a 1000 mL volumetric flask containing 600 mL of distilled water. Mix thoroughly by swirling.
4. After the polyvinyl alcohol solution has cooled to room temperature, add the 100 mL of polyvinyl alcohol solution to the nitric-acetic reagent. Allow the reagent to cool to room temperature and dilute to the 1000 mL mark with distilled water. Mix thoroughly by inversion.
5. Store the nitric-acetic/polyvinyl alcohol reagent in a tightly-stoppered container at room temperature. The reagent is usable for at least 12 months when stored as directed.

Chloride Measurement

6. Clean the electrodes and silver wire of the Chloridometer with silver polish.
7. Transfer approximately 6 mL of buffer reagent into the sample vial of the Chloridometer using the auto-dispenser.
8. Select the LOW or HIGH range setting of the Chloridometer depending on the anticipated chloride concentration. The HIGH range is usually selected for samples containing more than 200 mg/L chloride.
9. Set the titration switch to AUTO.
10. Set the blank adjust to ZERO.
11. Slide the sample vial up until the electrodes of the Chloridometer are immersed and the stirrer starts. Disregard the reading produced.
12. With the sample vial in the raised position, pipet a suitable volume of sample into the vial and record the reading when the titration is complete. The sample volume is selected using the anticipated chloride content and the table given in the calculations. The first reading with a fresh buffer is often erroneous and is rejected. Pipet three additional aliquots into the sample vial and record each reading. Average the values to obtain the chloride concentration. Repeat this step for subsequent samples.
13. The buffer does not require changing until the sample vial is full. At this time the sample vial is removed, the electrodes are rinsed with distilled water and dried with a Kimwipe (a).

Standby

14. The Chloridometer is set to STDBY when not in use. Do not leave electrodes immersed in the buffer reagent or sample.

Calculations: Multiply the reading obtained from the instrument by the appropriate factor depending on sample volume and instrument setting, according to the following table.

Sample Volume (mL)	Range Setting	Factor	Range (mg/L)
0.354	Low	1	5 to 200
0.354	High	10	50 to 2000
0.0354	Low	10	50 to 2000
0.0354	High	100	500 to 20000

Precision: Typical precision data associated with chloride determinations by this procedure are summarized below. Data was derived from 10 replicate readings on prepared NaCl standard solutions.

Mean Value (mg/L)	Standard Deviation (mg/L)	Relative Std. Dev.
11.7	±1.2	10.3%
977	±10	1.0%

Precision is mainly controlled by the repeatability of the pipetting step rather than the titration.

Comments:

a. The generating electrode will gradually wear thin. Once it is significantly smaller than the reference electrodes, remove the coil of silver wire, cut off the used end and reinsert the wire into the electrode assembly. Ensure that the generating electrode is the same length as the reference electrode and does not interfere with the stirrer.

Reference:

1. Buchler Instruments "Digital Chloridometer Model 4-2500 Instruction Manual." Fort Lee, N.J., 1974.

Determination of Surface and Interfacial Tensions by the Du Nouy Torsion Ring Method

Scope: This method measures the surface tension of both organic and aqueous solutions, and the interfacial tension of organic/aqueous phases. A technique for deriving the surface tension of bitumen at ambient temperature is also described.

Summary: The surface and interfacial tensions are determined by measuring the force necessary to detach a planar ring of platinum-iridium wire from the surface of the liquid. For interfacial tensions the ring is detached from the liquid of higher surface tension. The force is measured by a direct reading torsion-type balance. This reading is corrected by a factor which depends upon the force applied, the density of the solutions, and the dimensions of the ring.

Background: Surface and interfacial tensions provide information pertaining to the presence and concentration of surface active agents. These compounds play an important role in the performance of flotation and emulsion systems.

The surface tension of a liquid may be measured by a variety of methods. The present procedure is based on the Du Nouy torsion ring method. Since the surface tension affects the equilibrium shape of liquid surfaces, analysis of drop or bubble shapes may also be used to determine surface tension. In addition, the rise of liquid in a capillary may be determined and used to calculate the surface tension quite rapidly.

Surface tension measurements by the ring method carried out on whole bitumen below 60°C are inaccurate due to the viscous nature of bitumen. This problem is overcome by measuring the surface tension of several bitumen/solvent solutions at the desired temperature and extrapolating the resulting linear curve to whole bitumen. The preferred solvent is toluene.

Safety Considerations:

1. Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.
2. Methyl ethyl ketone — moderately toxic by inhalation and skin absorption. Extremely flammable.
3. Chromic Acid — strong oxidizing agent. Employ rubber gloves and a face shield.

Apparatus, Reagents, Materials:

1. Fisher Surface Tensiomat Model 21.
2. Calibration weight — 600 mg.
3. Glass cylindrical vessels having a minimum diameter of 50 mm. 100 mL beakers are satisfactory.
4. Hot plate.
5. Solvents:
   Acetone, A.C.S reagent grade
   Methyl ethyl ketone, A.C.S reagent grade
   Toluene, A.C.S reagent grade.
6. Chromic acid.
7. Supply of deionized water.

Procedure: Calibration of the Surface Tensiomat

1. The calibration of the Surface Tensiomat has been set at the factory but should be checked before use and adjusted if necessary. The calibration is carried out so that the dial will read directly in mN/m.

   Ensure that the torsion arm arrest mechanism is holding the arm. Hang the platinum-iridium ring on the hook at the left end of the lever. Cut a small strip of

paper and fit it onto the ring to act as a platform for a weight which will be used for the calibration. Release the torsion arm and adjust the torque applied to the ring until the index and its image are exactly in line with the reference line of the mirror. Turn the knob beneath the main dial on the front of the instrument until the vernier reads zero on the outer scale of the dial. Arrest the torsion arm.

2. Place a known weight on the paper platform (600 milligrams is suitable and simplifies calculations). Release the torsion arm. Adjust the torque applied to the ring until the index and its image are again exactly in line with the reference line of the mirror. Record the dial reading to the nearest 1/10 scale division by use of the vernier.

   It is now necessary to determine the accuracy of the calibration from the reading obtained. The apparent surface tension, P, is given as:

$$P = \frac{Mg}{2000L}$$

   where: M = the weight, g
   g = acceleration of gravity, m/s^2
   L = mean circumference of the ring, mm
   P = dial reading = apparent surface tension, mN/m

   The mean circumference of rings is 60.0 mm, but since slight deviations may be found, the circumference of each ring is noted on its container.

   If the dial reading differs from the calculated value, the effective length of the torsion arm must be adjusted until these two values agree. This adjustment is accomplished by turning the knurled knob at the left end of the lever arm so as to move the hanger hook. If the recorded dial reading is greater than the calculated value, move the hook to shorten the effective arm length. Conversely, if the dial reading is less than the calculated value, move the hook to lengthen the effective length of the arm. Repeat the calibration procedure until the dial reading and calculated value agree.

Determination of Surface Tensions

3. Great care must be taken to prevent contamination throughout the procedure. The glasswware is washed with toluene followed by several washes with methyl ethyl ketone and water. It must then be immersed in chromic acid and rinsed thoroughly with deionized water. The platinum-iridium ring is rinsed with toluene and methyl ethyl ketone, then heated in the oxidizing portion of a gas flame. All samples to be measured must be brought to the temperature of the experiment prior to reading.

4. Attach the ring to the hook at the end of the lever arm. Transfer the sample (minimum 50 mL) to a clean glass vessel and place it on the sample table. Move the sample table around until it is directly beneath the ring. Raise the sample table until the ring is immersed approximately 3 mm in the sample.

5. Release the torsion arm and adjust the instrument to a zero reading. Adjust the torque applied to the ring until the index and its image are exactly in line with the reference mark on the mirror. Be careful to keep the ring in the liquid during this manipulation, raising or lowering, if necessary, by means of the adjustment underneath the table. Now turn the knob beneath the main dial on the front of the case until the vernier reads zero on the outer scale of the dial.

6. Lower the sample table until the ring is in the surface of the liquid, while at the same time adjusting the torque applied to the ring to keep the index lined up with the reference mark on the mirror. The surface of the liquid will become distended but the index must be kept on the reference. Continue the two simultaneous adjustments until the distended film at the surface of the liquid breaks. The scale reading at the breaking point of the distended film is the apparent surface tension.

7. The surface tension of whole bitumen must be extrapolated from a plot of surface tension versus wt % bitumen in solvent. Prepare a series of samples (minimum 50 mL each) of various weights of bitumen in toluene. Determine the apparent surface tension of each sample and plot this value versus wt % of bitumen on rectangular coordinate paper. Correct bitumen weights for residual solvent content if obtained via a solvent extraction procedure (a). Determine the apparent surface tension of whole bitumen by extrapolation to 100% bitumen.

Determination of Interfacial Tension

8. Observe precautions to prevent contamination as outlined in Step 3. Attach the ring to the hook at the end of the lever arm.

9. Transfer the more dense liquid (minimum 50 mL) to a clean glass vessel and place it on the sample table. Move the table to enter the sample beneath the ring. Raise the table until the ring is immersed about 3 mm.

   Release the torsion arm and adjust the instrument to a zero reading. Adjust the torque applied to the ring until the index and its image are exactly in line with the reference mark on the mirror. Be careful to keep the ring in the liquid during this manipulation, raising or lowering the sample table, if necessary, by means of the knob adjustment underneath the table. Now turn the knob beneath the main dial on the front of the case until the vernier reads zero on the outer scale of the dial.

10. Introduce 20 to 30 mL of the less dense liquid onto the surface of the heavier liquid. The layer of lighter liquid should be deep enough so that the ring will not break through the upper surface of the lighter liquid before the interface film ruptures.

    Allow the interface to stabilize for 30 seconds.

11. Lower the sample table until the ring is in the interface between the two liquids, while at the same time adjusting the knob on the right side of the case to keep the index lined up with the reference mark on the mirror. The interface between the two liquids will become distended, but the index must be kept on the reference. Continue the two simultaneous adjustments until the distended film at the interface ruptures. The scale reading at the breaking point of the interfacial film is the apparent interfacial tension.

Calculations: The Surface Tensiomat measures apparent surface and interfacial tensions. In order to obtain absolute values, use the relationship:

$$S = P \times F$$

where S is the absolute value, P is the apparent value as indicated by the dial reading and the F is a correction factor. The correction factor F is dependent on the size of the ring, the apparent surface or interfacial tension, and the densities of the two phases. The relationships are expressed in the following forms, either of which may be used in preparing a correction factor chart in which the correction factor is plotted against $\frac{P}{D-d}$ for the R/r value characteristic of the ring used.

$$(F-a)^2 = \left[\frac{0.363}{(\pi R)^2}\right]\left[\frac{P}{D-d}\right] + K$$

$$F = 0.7250 + \sqrt{\frac{1.452\ P}{C^2\ (D-d)} + K}$$

where: F = the correction factor
R = the radius of the ring, mm
r = the radius of the wire of the ring, mm
P = the apparent surface or interfacial tension, mN/m
D = the density of the lower phase, kg/L
d = the density of the upper phase, kg/L
K = 0.04534 − 1.679 r/R
C = the circumference of the ring, mm
a = 0.725

The numerical part of K and a are universal constants for all rings.

Precision: Evaluations to determine the precision of surface tension measurements on aqueous and organic samples have not been undertaken. ASTM D 971 for the measurement of interfacial tension of oil against water quotes repeatability and reproducibility values of 2% and 5% of the mean, respectively.

Comments: a. For example the determination of residual toluene is incorporated in Method 2.7.

References:

1. Fisher Surface Tensiomat Model 21 Instruction Manual.
2. ASTM. "Interfacial Tension of Oil Against Water by the Ring Method." Annual Standards (1976), Part 23, Method D 971.

Determination of Electrophoretic Mobility and Zeta Potential of Colloid Particles

Scope: This method determines electrophoretic mobility and Zeta potential of colloid particles in aqueous systems.

Summary: The electrophoretic mobility and Zeta potential are both measured using a Zeta-Meter electrophoresis cell. The sample is introduced to the electrophoresis cell and a suitable direct current voltage, usually between 100 and 400 volts,is applied. The time required for a colloid particle to traverse a fixed distance in the direction of the anode or cathode, as viewed under a microscope, is measured. The observed time is then converted to electrophoretic mobility. Zeta potential values are determined through application of the Helmholtz-Smoluchowski formula.

Background: By definition, electrophoretic mobility is the velocity of a colloid species in an electric field of 100 V/m. Zeta potential affords a measure of the electrokinetic charge surrounding the suspended particulates and is considered to be the basic principle governing colloid stability. According to the Helmholtz-Smoluchowski formula the Zeta potential is given by:

$$ZP = 3600\ \pi \frac{n_t}{E_t} EM$$

where: ZP = Zeta potential of the suspended particles, mV
n_t = viscosity of suspending liquid at the measurement temperature, Pa·s
E_t = dielectric constant of the suspending liquid at the measurement temperature
EM = electrophoretic mobility in μm/s per 100 V/m

The theory and associated limitations of the Helmholtz-Smoluchowski equations are described elsewhere (1-3).

The stability of a colloid system or emulsion is dependent upon adsorption of ions or surfactants from the bulk of the suspending material. Zeta potential provides information about the adsorption mechanism and subsequent monitoring to achieve the desired process condition. In the case of hot water flotation of oil from oil sand, it is desirable to maintain colloid stability. Colloids that flocculate may trap oil that would otherwise be available for flotation and result in decreased oil recovery. The method is also useful for indicating flocculant dosages, if such chemicals are used to treat tailings.

The electrophoresis cell has several inherent limitations that may affect the accuracy of electrophoretic mobility and Zeta potential measurements of systems having high specific conductance. The high voltages that are usually employed may result in thermal overturn. This occurs when the temperature of the liquid in the cell increases and causes convection currents. As a result, the colloid will travel in a spiral instead of a straight line and cannot be tracked. This problem can be resolved by reducing the applied voltage. However, the voltage must not be decreased to such an extent that the rate of particle migration is so slow as to allow the particles to settle out and disappear from view in the microscope. Generally for precise work several particles are tracked and the average time is used for the calculations.

The Zeta-Meter equipment employed in this method and the graphs for computing results have not been illustrated in this method. They are described elsewhere (2,3).

Safety Considerations: The operator should always guard against electric shock. When the Zeta-Meter is unattended, the power unit should always be turned off, or the power cable removed. The instrument has been designed for safe operation and it is not possible for the operator to receive shock if the following precautions are observed:

1. Never touch both platinum electrodes or both leads simultaneously. That is, never touch one electrode or lead with one hand and simultaneously touch the

other electrode or lead with the other hand. When attaching or removing electrodes, always keep one hand below the table.

2. Do not touch or handle the electrodes or leads except under the following conditions:
   i) The DC VOLTAGE control knob must be in the OFF position
   ii) The VOLTAMETER must read zero
   iii) The DC POLARITY switch must be in the center OFF position

Apparatus, Reagents, Materials:

1. Zeta-Meter — complete with accessories including: clear plastic eletrophoresis cell with iridium hardened electrodes and stoppers, microscope illuminator with blue filter, heat absorbing cell holder for reflecting illuminator beam through the cell tube, and stereoscopic microscope with mechanical stage and ocular micrometer. Zeta-Meter Inc., 1720 First Avenue, New York, NY 10028.
2. High speed centrifuge — 333 rev/s max., 39000 x G, 8 x 52 mL capacity, 8 place angle head.
3. Steel centrifuge tubes — 50 mL, with caps.
4. Manual Timer.
5. Pipe cleaners.

Procedure:

Sample Preparation

1. Approximately 50 mL of sample are required to fill the cell. If samples appear dirty, as in the case of fine clay slurries, centrifuge at 250 rev/s for 20 minutes and decant the clear liquid for analysis (a). Ensure the sample is at room temperature and record the sample temperature.

Cleaning the Cell

2. Clean the cell, electrodes, and stoppers daily with a sponge, immersing them in warm water containing soap or a mild detergent. The interior of the sol-chambers may be cleaned with a piece of wet Kimwipe. Clean the cell tube, electrodes and stoppers copiously with deionized water having about the same temperature as the sample.

Filling the Cell

3. To fill the cell, lightly insert the two tapered stoppers in the ends of the cell tube. Hold the cell over a sink, and pour the sample into the left hand sol-chamber until the right hand chamber is about half full. Then rotate and loosen each of the stoppers to produce a drip and force the air bubble from each end of the cell tube. Retighten the stoppers very firmly. Again pour the sample into the left hand sol-chamber until the right hand chamber overflows.
4. Carefully insert the platinum electrode in the left hand sol-chamber. Use a strong downward twisting motion to secure the stopper. Care should be exercised that not even one small air bubble is left under the stopper. If this occurs, remove the stopper, refill the cell to overflowing, and re-insert the stopper. Pour off the right hand sol-chamber until the liquid level is 6 mm below the rim. Insert the flat electrode. If the liquid level is high enough to reach the electrode where it lies flat against the interior sol-chamber wall, siphonage will result. Wipe the outside of the cell dry with a towel.

Operation of the Zeta-Meter

5. Position the cell holder on the mechanical stage of the microscope and place the cell with sample on the holder. The cylindrical electrode should be on the operator's left and the strip-type electrode on the right. Adjust the stage to position the center of the cell tube directly beneath the optical axis of the microscope.

6. Set the voltage to the illuminator at 6.5. Focus a thin beam of light downward through the plate glass cell holder to its mirror back. This beam is reflected upward and passes through the cell, causing reflecting colloids to be seen as tiny rays of light.

7. Employing the 2X objective, focus the microscope so that the positioning line of the cell is clear and distinct. In sharp focus this line marks the horizontal plane which passes through the exact center of the cell tube. The nosepiece is then rotated to the 6X position and the mechanical stage is traversed toward the front or rear until the positioning line coincides with the OX----OX line of the ocular micrometer. The microscope should again be focussed for maximum clarity and sharpness of the positioning line. Adjust the voltage to the illuminator until the colloids in the cell are plainly visible.

8. The alligator clips attached to the DC output leads should then be connected to the platinum cell electrodes, with the red (positive) lead at the operator's left and the black (negative) lead at the operator's right. Use the left hand to make the red connection. Then use the right hand to make the black connection. Do not use both hands simultaneously. Set the DC POLARITY to NORMAL.

9. Apply a direct current voltage of 100 to 400 V to the cell. Electronegative colloids and suspensoids will migrate toward the positive terminal (anode) on the left. If the particles have no charge they will remain stationary. If they are positively charged they will migrate toward the negative terminal (cathode) on the right. The voltage employed should be such as to give a time interval of about 3 to 6 seconds for traverse of one ocular division by a particle.

   High Zeta potential values are best tracked at 100 to 200 V, and low Zeta potential values at 300, 400 or even 500 V. Voltage is limited by the conductivity of the sol. High voltage results in high wattage input, which may heat the liquid in the cell tube and cause thermal overturn, i.e. particles move in directions other than towards an electrode. If overturn is visually evident, voltage must be reduced to as low as 50 V if required. Very low Zeta potentials may require time intervals of 10 to 100 seconds for one ocular micrometer division.

10. Discrete particles on or near the counting line for the objective employed are then timed in their traverse of one or more ocular micrometer divisions using the manual timer. Five to ten discrete particles should be timed in their normal direction of travel. Reverse the DC POLARITY and time the movement of five to ten particles in the opposite direction. Do not time either the fastest or slowest moving colloids, but select those which appear to be moving at average velocity. Track only particles in sharp focus.

11. The cumulative time in seconds for migration in both directions is divided by the total number of ocular micrometer spaces traversed to obtain the average time required for a particle to traverse one micrometer division. Also record the voltage applied across the cell, the objective magnification, and the final temperature of the sample. Take the average of the initial and final temperatures as the sample temperature.

Calculations:

1. Calculate $N = \frac{\text{Objective Magnification x Voltage}}{100}$

2. From the graph supplied with the Zeta-Meter, interpolate the electrophoretic mobility from the average time for a particle to traverse one micrometer division and N. Include the temperature correction to 25°C in the determination of the electrophoretic mobility.

3. If the migration of particles was towards the left when the DC POLARITY was in the normal position, the electrophoretic mobility is reported as negative, indicating that the particles are electronegative. If migration was towards the right, report the electrophoretic mobility as positive. The units of electrophoretic mobility are μm/s per 100 V/m.

4. Using the graph supplied with the Zeta-Meter interpolate the Zeta potential from the electrophoretic mobility at 25°C (b). If necessary extrapolate for electrophoretic mobilities not given. If the electrophoretic mobility is negative, report the Zeta potential as negative and vice versa. Zeta potential is reported in mV.
5. Report the electrophoretic mobility and Zeta potential to the nearest whole unit, with the appropriate sign.

Precision: Actual differences in the electrophoretic velocities of individual colloidal particles constituting the system, and consequently the ability of the operator to select colloids of intermediate speed for tracking, results in considerable variation among time measurements. With an experienced operator, the precision of electrophoretic mobility and Zeta potential measurements on replicate samples from a common source (based on tracking a minimum of 10 particles per sample) is typically 10-20% relative.

Comments:

a. The sample must not be diluted. The sample may be filtered through a 0.45 μm filter if further clarification is required.
b. The viscosity and dielectric constant for water at 25°C are assumed in the calculation of Zeta potential.

References:

1. Adamson A.W. Physical Chemistry of Surfaces. 2nd Ed. Interscience, 1967.
2. Riddick T.M. Control of Colloid Stability Through Zeta Potential. Vol. I, Zeta-Meter Inc., 1968.
3. Zeta-Meter Inc. Zeta-Meter Manual 2nd Ed. New York, NY, 1968.

Determination of Bitumen, Water and Solids Content of Oil Sand, Reject and Slurry Samples (Classical)

Scope: This method determines the bitumen, water and solids content of oil sand and reject samples initially prepared by Methods 1.2, 1.3, or 1.4. The method also applies to slurry samples.

Summary: The sample is separated into bitumen, water and solids by refluxing with toluene in a solids extraction apparatus. Condensed solvent and co-distilled water are continuously separated in a trap, the water being retained in the graduated section. The solvent recycles through the extraction thimble of the extraction apparatus to dissolve the bitumen. The resulting bitumen/solvent and non-filtered solids fractions are subsequently separated by centrifuging. An aliquot of the bitumen extract is evaporated to remove the solvent. The bitumen is measured gravimetrically and a correction is applied for residual toluene content. The solids are also determined gravimetrically by combining the contributions for solids retained by the extraction thimble and for the non-filtered solids.

Safety Considerations:

1. Hydrochloric acid — highly toxic by inhalation. A strong irritant to the eyes and skin.
2. Isopropyl alcohol — irritant to skin and respiratory tract. Highly flammable.
3. Toluene — moderately toxic by skin absorption and inhalation. Possesses irritant and anesthetic properties. Highly flammable.
4. Trichlorethylene — a suspected carcinogen. Employ strict precautions to prevent any inhalation or skin absorption.

Apparatus, Reagents, Materials:

1. Condenser — a straight tube condenser having a water jacket at least 400 mm long. West type condenser with 24/40 standard taper joint as specified in ASTM E 123 is suitable.
2. Water trap — the trap having 24/40 standard taper joints shall be of 10 mL capacity for oil sand and reject analyses or 25 mL capacity for slurry analyses. The designs are taken from ASTM E 123. The 10 mL trap has 0.1 mL scale divisions and a maximum scale error of 0.05 mL. The 25 mL trap has 0.1 mL scale divisions and a maximum scale error of 0.05 mL from 0 to 1 mL. From 1 to 25 mL, scale divisions are 0.2 mL with a maximum scale error of 0.1 mL.
3. Kettle — a heat-resistant glass vessel having a nominal capacity of 500 mL. The neck shall be a minimum of 250 mm long, including a 55/50 standard taper female joint to accommodate a kettle-to-trap adapter.
4. Kettle-to-trap adapter — the lower part of the adapter has a 55/50 standard taper male joint with a perforated downcomer extending below the ground glass surface. The upper part of the adapter is fitted with a 24/40 standard taper female joint.
5. Extraction thimble — Whatman 43 x 123 mm cellulose thimble, single thickness for oil sand and reject analyses or double thickness for slurry analyses.
6. Thimble basket — a corrosion-resistant basket to support the thimble. See Figure 1. Fabrication from 1.5 mm diameter nichrome or chromel wire using a silver solder bottom joint is suitable.
7. Solvent distributor — a corrosion-resistant screen to snugly fit over the open end of the thimble.
8. Heating mantle — 250 W, to accommodate 500 mL kettle.

The assembled extraction apparatus is shown schematically in Figure 2.

9. Kimwipes — Type 900-S.

10. Weighing bottles — short form, 50 x 140 mm of borosilicate glass, with a 55/12 ground glass rim.
11. Centrifuge — 87 rev/s max, 4275 x G, 6 x 1000 mL capacity, complying with Class 1 Group D explosion-proof requirements, and equipped with an eight place horizontal head, trunion rings and shields.
12. Centrifuge tubes — 100 mL, conical, graduated as described in ASTM D 96.
13. Volumetric flasks — 10, 100, and 250 mL, Class A.
14. Transfer pipet and bulb — 50 mL, Class A.
15. Evaporating dishes — 120 mL, porcelain.
16. Graduated cylinders — 5 and 10 mL.
17. Syringe — 2 mL.
18. Double beam infrared spectrophotometer.
19. Sodium chloride cells — 0.5 mm path length, matched.
20. Top loading balance to $\pm$0.001g, 320 g capacity.
21. Drying oven — forced draft, set at 120°C.
22. Desiccator.
23. Reagents:
    Hydrochloric acid, A.C.S. reagent grade.
    Isopropyl alcohol, A.C.S. reagent grade.
    Toluene, A.C.S. reagent grade.
    Trichloroethylene, A.C.S. reagent grade.

Sample Handling

1. Sample sizes should range from 40 to 50 g.
2. Prior to use, insert 3 rolled Kimwipes into each of a quantity of new thimbles. Prepare single thickness thimbles for oil sand and reject analysis or double thickness thimbles for slurry samples. Place each thimble in a weighing bottle and dry, uncapped, for 1 hour at 120°C. Cap the weighing bottles and store in a desiccator until needed.
3. Weigh the weighing bottles plus thimbles to the nearest 0.001 g. Remove the Kimwipes and place the thimble in its support basket. Mount the thimble and basket in the neck of the kettle by spreading the basket's attaching wires. Clean the outside of the sample container and weigh to the nearest 0.01 g. Transfer the sample to the thimble, wash with small amounts of toluene until clean, and wipe dry with the Kimwipes. Before transferring slurry samples, add 0.5 mL hydrochloric acid to the sample. Place the Kimwipes in the thimble. Weigh the empty sample container.
4. Add approximately 120 mL toluene to the kettle. Cover the thimble with the solvent distributor and attach the basket to the adapter. Assemble the apparatus as in Figure 2, ensuring all connections are vapour tight. Use the 10 mL trap for oil sand and reject samples, and the 25 mL trap for slurry samples. Do not use grease on the ground glass surfaces (a).

Extraction

5. Apply heat and adjust to maintain the reflux rate such that liquid does not overflow the thimble. Continue refluxing for 30 minutes after no water is visible in any part of the apparatus except the trap, and the solvent dripping from the thimble is colorless. Discontinue heating and when refluxing has stopped add three drops of isopropyl alcohol around the inside rim of the condenser to bring water droplets adhering to the glass surface of the condenser down into the trap.

Water

6. Allow the trap and contents to cool to room temperature. Estimate the volume of water in the trap to the nearest 0.01 mL for oil sand and reject, and to the nearest 0.05 mL for slurry. Subtract 0.5 mL from the water volume of the slurry samples to account for the hydrochloric acid addition.

Solids

7. Disassemble the apparatus, remove the thimble from its support and return it to its original weighing bottle. For oil sand and slurry dry the thimble, uncapped, for eight hours at 120°C. For rejects dry for 10 hours. Cool the capped assembly in a desiccator and weigh to the nearest 0.001 g.

Bitumen and Non-filtered Solids

8. Transfer the toluene solution of bitumen and fine particles which passed through the thimble to a 250 mL volumetric flask. Dilute to volume with toluene. Invert the flask several times to suspend the non-filtered solids and immediately decant 75 mL to a centrifuge tube preweighed to 0.001 g. Spin at 33 rev/s for 20 minutes. Transfer a 50 mL aliquot of the resulting bitumen/solvent solution to a porcelain evaporating dish preweighed to 0.001 g. Discard the remaining liquid in the centrifuge tube. Wash the inner walls of the tube with toluene, being careful not to dislodge the solids present. When clean, dry the centrifuge tube plus solids at 120°C for 1 hour. Cool in a desiccator and weigh.

9. Allow the bitumen/solvent solution contained in the dish to evaporate until the residual solvent content is between 1 and 5%. The bitumen at this point flows very slowly when the dish is tipped. Weigh the dish plus bitumen and proceed with step 11 to detemine the residual toluene content.

Preparation of Residual Toluene Calibration Curve.

10. Prepare a 100 mL stock solution of 20 g benzene-extracted bitumen in trichloroethylene and a 5 mL stock solution of 1.00 g toluene in trichloroethylene.

    Prepare a series of standard solutions by combining the required volumes of toluene stock solution with sufficient bitumen stock solution in 10 mL volumetric flasks, as outlined in the following table.

Toluene Concentration (wt%)	Volume of Toluene Stock Solution (mL)
0.5	0.05
1.0	0.10
2.0	0.20
3.0	0.30
4.0	0.40
5.0	0.50
7.0	0.70
10.0	1.00

    Ready the infrared spectrophotometer. Fill the reference cell with trichloroethylene and place in the reference beam. Fill the sample cell with each calibration standard and record the scans from 770 to 665 cm^{-1}. Flush the sample cell with trichloroethylene and air dry between each scan.

    Construct a baseline by drawing a straight line tangent to the shoulders of the absorption peak at approximately 699 cm^{-1}. See Figure 3. Calculate the net absorbance of this peak by subtracting the baseline absorbance from the gross absorbance of each standard.

    Prepare a calibration curve by plotting the net absorbance of each standard versus its wt % toluene on rectangular coordinate paper. Draw the best fit through the points.

Residual Toluene Determination

11. Calculate the amount of trichloroethylene required to form a final volume numerically equivalent to 5 times the weight of bitumen retained in the evaporating dish.

    Add approximately half this volume to the sample to dissolve the bitumen and transfer the solution to a 5 or 10 mL graduated cylinder. Clean the dish with small washes of trichloroethylene, adding the rinses to the cylinder. Dilute to the volume calculated above and charge a portion to the infrared cell.

    Scan the sample from 770 to 665 cm^{-1} and determine the net absorbance of the peak at 699 cm^{-1}.

    Obtain the weight % residual toluene in the sample from the calibration curve.

Calculations:

1. The bitumen, water and solids contents of oil sand and slurry samples are given by:

$$\% \text{ Bitumen} = \frac{B}{W} \times 100$$

$$\% \text{ Water} = \frac{V}{W} \times 100$$

$$\% \text{ Solids} = \frac{S + 3.33A}{W} \times 100$$

2. The bitumen, water and solids contents of reject samples are given by:

$$\% \text{ Bitumen} = \left(\frac{B}{W}\right)(100 - L)$$

$$\% \text{ Water} = \left(\frac{V}{W}\right)(100 - L) + L$$

$$\% \text{ Solids} = \left(\frac{S + 3.33A}{W}\right)(100 - L)$$

where:
- V = volume of water retained in trap, mL. The density of water is assumed to be 1.0 kg/L.
- W = sample weight, g
- S = weight of solids recovered in thimble, g
- A = weight of fines recovered in centrifuge tube, g
- B = 5R(100 − T)/100 = total bitumen weight, g
- R = weight of bitumen and residual toluene in evaporating dish, g
- T = weight % residual toluene
- L = weight % water loss as determined by Method 1.4.

Precision: Typical values relating the precision of an oil sand determination are tabulated below for three oil sand grades. Each data set was derived from the analysis of 10-30 replicate subsamples obtained from a larger quantity of oil sand prepared as described in Method 1.2. Hence, precision values indicated include the variance due to subsampling. Estimates for the precision of reject and slurry analyses have not been determined.

Lean Oil Sand	Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
Bitumen	10.09	±0.17	1.68%
Water	3.70	±0.24	6.49%
Solids	86.21	±0.30	0.35%
Bitumen	7.47	±0.22	2.95%
Water	0.50	±0.15	30.00%
Solids	91.84	±0.18	0.20%

Medium Oil Sand			
Bitumen	11.65	±0.14	1.20%
Water	2.17	±0.87	40.09%
Solids	86.18	±0.84	0.97%
Bitumen	11.48	±0.23	2.00%
Water	2.64	±0.31	11.74%
Solids	85.50	±0.22	0.26%
Rich Oil Sand			
Bitumen	14.44	±0.12	0.83%
Water	0.36	±0.21	58.33%
Solids	85.20	±0.25	0.29%
Bitumen	13.95	±0.25	1.79%
Water	0.39	±0.19	48.72%
Solids	85.56	±0.20	0.23%

Comments: a. Grease interferes with the infrared determination of the residual toluene.

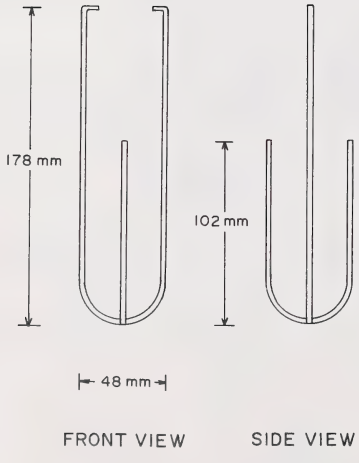


FIGURE 1: EXTRACTION THIMBLE BASKET

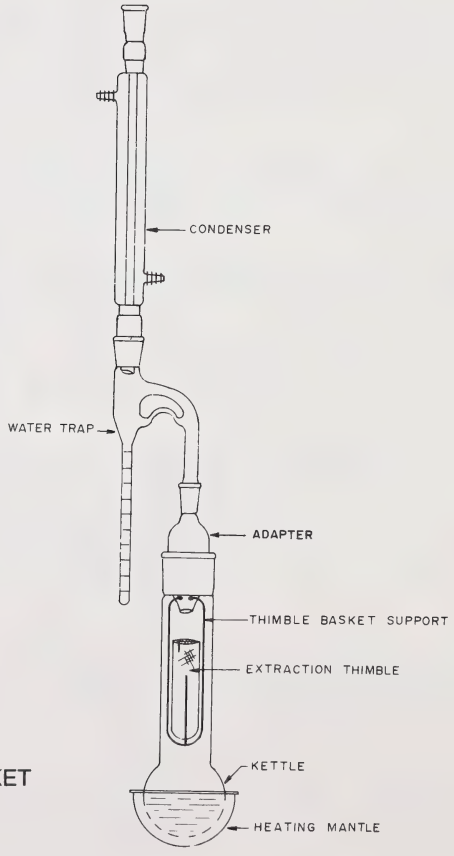


FIGURE 2: EXTRACTION APPARATUS

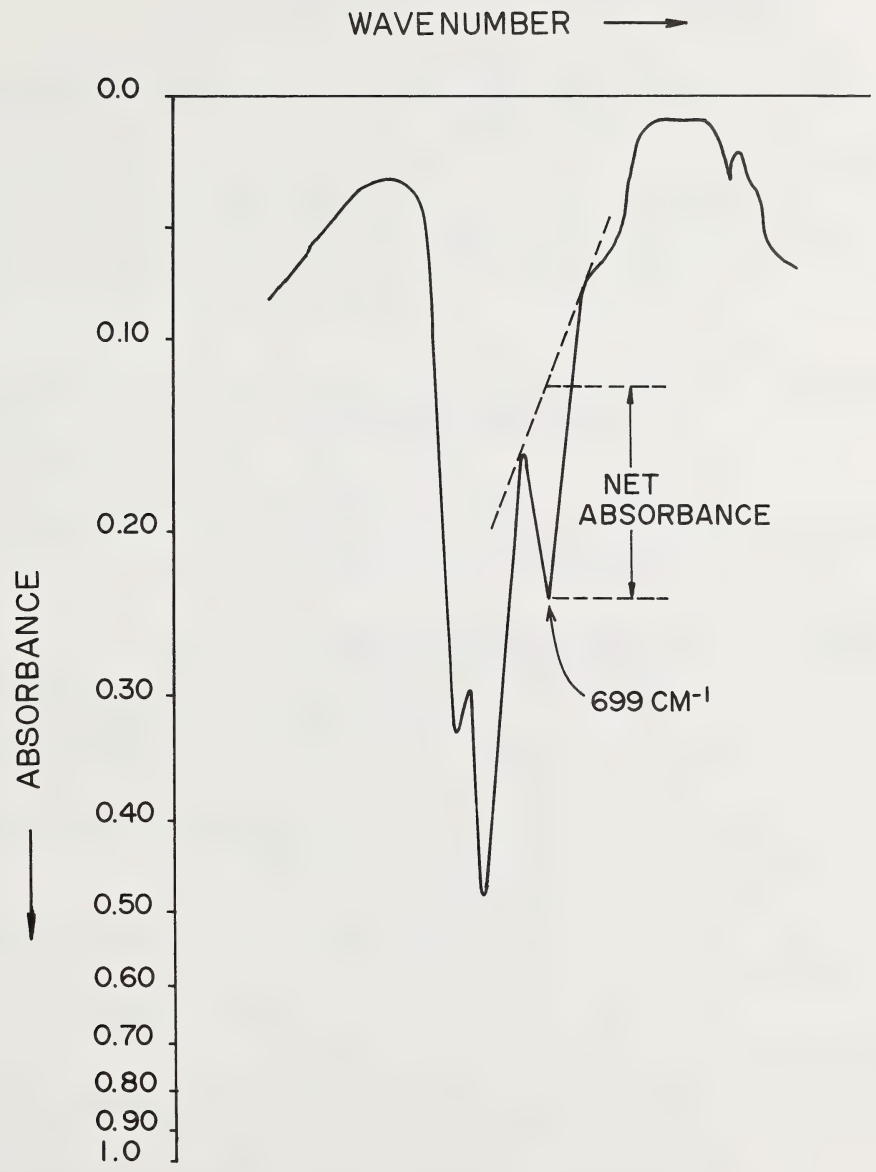


FIGURE 3: MEASUREMENT OF NET ABSORBANCE AT 699 CM^{-1}
FOR RESIDUAL TOLUENE DETERMINATION

Syncrude Method For the Determination of Bitumen, Water and Solids Content of Oil Sand and Rejects

Scope: This method determines the bitumen, water and solids content of 20 - 50 g of oil sand initially prepared by Methods 1.2 or 1.3. The method is also applicable to reject samples prepared by Method 1.4.

Summary: The bitumen and water in the sample are extracted from the oil sand or reject by shaking the sample with a known quantity of solvent. The solvent, a 74% toluene/26% isopropyl alcohol blend, dissolves both the bitumen and water in the sample. An aliquot of this extract is evaporated to remove the solvent and water, and the bitumen is determined gravimetrically. Another aliquot of the extract is analyzed for water content by an automatic Karl Fischer titration. The solids are filtered, dried, and weighed for a mass balance check.

Safety Considerations:

1. Dimethyldichlorosilane — evolves toxic and corrosive fumes of hydrogen chloride upon contact with moisture. Avoid contact with skin, eyes, or clothing; do not breath fumes. Neutralize excess reagent by cautious addition of methanol.
2. Isopropyl alcohol — irritant to the skin and respiratory tract. Highly flammable.
3. Karl Fischer reagent — toxic by skin absorption and inhalation. Flammable.
4. Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.

Apparatus, Reagents, Materials:

Extraction, Bitumen Determination, Water Determination

1. Nalgene linear polyethylene bottles — 500 mL capacity for oil sand and 250 mL capacity for rejects, with polypropylene screw closures. Nalge 2104.
2. Reciprocating shaker — 40 mm stroke, set at approximately 5 cycles/s, and equipped with carrier.
3. Centrifuge — 87 rev/s max., 4275 x G, 6 x 1000 mL capacity, complying with Class 1, Group D explosion-proof requirements, equipped with six place horizontal head and 250 mL aluminum cups.
4. Syringe — 10 mL, glass, Luer-Lok tip.
5. Disposable filter assemblies — Millipore Millex filters, 0.45μm, 25 mm diameter, catalogue no. SLHA 025 OS.
6. Erlenmeyer flasks — 25 mL, with ground glass tops fitted with ground glass stoppers.
7. Transfer pipet — 5 mL, Class A, with bulb.
8. Glass fiber filters — 150 mm diameter. Reeve Angel grade 934 AH.
9. Petri dishes — 100 mm diameter, 10 mm height.
10. Drying rack — a horizontal rod suspended between two retort stands which are approximately 1 m apart. Ten 20 mm foldback clips are hung on the rod.
11. Photovolt Aquatest II Automatic Karl Fischer Titrator and accompanying vessel and generator solutions. Photovolt Corporation, 1115 Broadway, New York, NY 10010.
12. Push button adjustable syringe — 200 μL. Hamilton CR700-200.
13. Densimeter — readable to ±0.0001 kg/L. Method 3.6 describes the use of a suitable densimeter.
14. Balances:
    Top loading balance to ±0.01 g, 1200 g capacity.
    Analytical balance.

15. Drying oven — forced draft, set at 110°C.
16. Desiccator.
17. Reagents:
    Isopropyl alcohol, 99 mol %
    Toluene, A.C.S. reagent grade.
18. Molecular sieves — type 4A.

Solids Determination

1. Filtering funnel — Buchner type with fine fritted disc, 350 mL capacity. Corning 36060.
2. Filtering flask — Erlenmeyer with side arm, heavy walls, 2000 mL capacity. Corning 3560.
3. Vacuum pump and tubing — 8.3 L/s free air capacity.
4. Reagents:
    Acetone, A.C.S. reagent grade
    Filter aid, Celite 499.

Preparation of Water Standards

1. Six serum bottles — 125 mL, with Viton flange type stoppers and aluminum seals.
2. Six volumetric flasks — 100 mL, Class A.
3. Reagents:
    Dimethyldichlorosilane (DMDCS)
    Methanol, A.C.S. reagent grade, dry.
4. Distilled water.

Preparation Steps: Solvent Blend Preparation

1. Fill a large closed container with 74% toluene and 26% isopropyl alcohol (volume %).
2. Add molecular sieves, type 4A, to the container and allow the solvent blend to dry for 24 hours. If the weather is unusually humid a longer drying time is required. Absolutely dry solvent (no reading on a Karl Fischer titrator) should be used to prepare the water standards so that their absolute water content will be known. However, a small residual water content (35 μg in a 100 μL injection into the Karl Fischer titrator) can be tolerated for sample analysis as long as this solvent blank value is known and is subtracted from the sample water reading.
3. Determine the density of the blend (Method 3.6). A 74% toluene/26% isopropyl alcohol blend has a density of 0.8440 kg/L at 20°C. If the density falls outside the range of 0.8435 to 0.8445 kg/L adjust the solvent blend as follows:
    i) For densities greater than the permitted range, add isopropyl alcohol until the correct density is obtained.
    ii) For densities less than the permitted range, add toluene until the correct density is obtained.

Preparation of Water Standards

4. All glassware used is first treated with the silylating agent DMDCS to prevent adsorption of water on the glassware for the standard solutions.
    i) Clean volumetric flasks and serum bottles with a strong detergent. Rinse well with water and then with acetone. Dry in oven and desiccate until cool.
    ii) Immerse glassware in a 5 to 10% DMDCS solution (in toluene) for a few minutes. Rinse glassware with dry methanol, dry in oven and desiccate until cool. Keep glassware stoppered with stoppers or septa which have also been dried in a desiccator. Hydrogen chloride is liberated from DMDCS on contact with moisture. Therefore, work in a fumehood and use gloves. Any DMDCS spills are easily neutralized with methanol.

5. Prepare six standard water solutions by weighing distilled water (to the nearest 0.0001 g) into 100 mL volumetric flasks. The solutions should contain approximately 0.25, 0.50, 0.80, 1.20, 1.60, and 2.00 g of water respectively. Use the dry 74% toluene/26% isopropyl alcohol blend as the solvent for these standard solutions. Mix the solutions well and transfer them to the prepared serum bottles. Immediately stopper and seal the bottles. These solutions should keep for several months.

Calibration of the Karl Fischer Titrator

6. The Aquatest II Karl Fischer titrator and syringe should be calibrated daily. Adjust the syringe so that it delivers a volume of about 100 μL. Do not change this volume between running the standard and sample solutions on the titrator.

7. Rinse the syringe three times with the most dilute water standard. Allow a few minutes to ensure that the chamber of the syringe is at its equilibrium volume, fill the syringe and inject an aliquot into the titration cell of the instrument. Flip the switch to TITRATE and record the number displayed when the END light comes on. Zero the display on the titrator, refill the syringe with the same standard solution, inject this aliquot into the titration cell and record the reading from the titrator. Titrate a third aliquot of the standard solution in the same manner. Then repeat this entire procedure for each successive standard solution. Determine the median titration value for each water standard. If the water readings for the 0.80 g of water standard vary by more than 15 μg check instrument and syringe performance.

Pipet Calibration

8. Calibrate a 5 mL transfer pipet with a solution of bitumen and water in the solvent blend which approximates the extract obtained in this method. Use only this pipet for the determination of bitumen. Calculate a pipet factor:

$$\frac{\text{volume of solution delivered by 5 mL pipet}}{5.0}$$

where the volume of the solution delivered is determined from the weight and density (Method 3.6).

Procedure:

1. Measure the density of the solvent blend daily. The permitted range is 0.8435 to 0.8445 kg/L. Inject 100 μL of the solvent blend into the Karl Fischer titrator. Any reading greater than zero must be subtracted from subsequent sample readings.

2. Weigh an empty Nalgene bottle (500 mL capacity for oil sand, 250 mL capacity for reject) to the nearest 0.01 g.

3. Weigh the sample container to the nearest 0.01 g. Transfer the sample to the Nalgene bottle. Use approximately 30 g into a 500 mL bottle for oil sand samples and 30 g into a 250 mL bottle for reject samples. Remove all traces of moisture from the sample container by washing it with a small quantity of the solvent blend. Pour these washings into the Nalgene bottle. When the sample container is dry, weigh it to the nearest 0.01 g.

4. Add approximately 250 mL of solvent blend to the Nalgene bottle for oil sand samples and 100 mL for reject samples. Weigh the bottle to the nearest 0.01 g. Tightly cap the Nalgene bottle.

Extraction

5. Place the Nalgene bottle containing the sample and solvent on its side on the reciprocating shaker. Allow the mixture to shake for 15 minutes for oil sand samples and 60 minutes for rejects. This extraction time is not critical as long as it is greater than 10 minutes for oil sand samples and greater than 60 minutes for rejects. For reject samples place the 250 mL Nalgene bottle in a centrifuge cup, ensure balance and centrifuge at 33 rev/s for at least 40 minutes. The long centrifuge time is required due to large quantitites of fine solids in reject material.

Water Determination

6. For oil sand samples, remove the Nalgene bottle from the shaker and allow the sample to settle for one minute. Rinse the Hamilton syringe three times with the sample extract solution. As in the calibration procedure allow a few minutes before filling the syringe with the aliquot to be titrated. Then shake the sample extract again, allow a minute for the coarse solids to settle, fill the syringe, and inject this aliquot into the titrator. Flip the titrator switch to TITRATE. When the END light comes on record the value of the aliquot titer.

   For reject samples, remove the sample from the centrifuge and rinse the Hamilton syringe three times with the sample extract solution. As in the calibration procedure, allow a few minutes before filling the syringe with the aliquot to be titrated. Refill the syringe and inject the aliquot into the titrator. Flip the titrator switch to TITRATE. When the END light comes on record the value of the aliquot titer.

Bitumen Determination

7. Dry the glass fiber filters by placing an open box of filters in an oven at 110°C for 1 hour. Cool them in a desiccator. Number the filters and weigh to the nearest 0.0001 g. (a)

8. The aliquot for the bitumen analysis of oil sand can be taken once the Nalgene bottle has been off the shaker 10 minutes or longer. Insufficient settling time can result in problems during filtration due to a large amount of suspended solids. The aliquot for reject bitumen assay can be taken immediately. Rinse a 10 mL syringe with the sample extract. Withdraw approximately 7 mL of the extract and attach a 0.45 μm Millipore Millex filter assembly to the syringe. Filter the extract into a 25 mL Erlenmeyer flask. Stopper the flask if the solution aliquot is not to be taken immediately. Rinse the 5 mL transfer pipet with the extract solution. Support a weighed glass fiber filter on a Petri dish. Pipet a 5 mL aliquot of the solution onto the weighed filter by continuously moving the pipet to disperse the extract evenly on the filter surface. Hang the filter from the drying rack to evaporate the solvent. The time required to dry the filter is critical and is selected using a 74% toluene/26% isopropyl alcohol solution of known bitumen concentration. Five mL aliquots are applied to filters and these are weighed at varying times. The time which gives the correct bitumen weight is selected for sample analysis. This drying time is approximately 15 minutes and need only be determined for the particular laboratory conditions in use. Weigh the filter with the bitumen.

Solids Determination

9. Fill the filtering funnel with enough Celite 499 to make a loosely packed layer approximately 30 mm thick, covering the entire surface of the glass frit. Weigh the funnel plus Celite 499 to the nearest 0.01 g.

10. Set up the filtering funnel and flask and attach to the vacuum outlet. Slurry the Celite 499 with toluene. Turn on the vacuum and decant the sample extract from the Nalgene bottle into the funnel. When most of the extract has filtered through, pour any remaining extract and solids into the funnel.

11. Wash the inside of the Nalgene bottle with solvent blend and pour the washings into the filter funnel to clean the solids. Gently pass air into the Nalgene container to dry it out. Then tap any remaining solids into the filter funnel.

12. Wash the solids in the funnel with several portions of solvent blend until all the bitumen has been removed (effluent appears clear). Then wash the clean solids with acetone to aid in drying. Leave the vacuum on for 3 or 4 minutes to remove most of the acetone from the solids.

13. Place the filter funnel containing the solids in the oven (110°C) for approximately 45 minutes to ensure complete drying, allow to cool, then weigh.

Calculations:

1. The Karl Fischer titrator calibration data is subjected to linear least squares regression to obtain the slope and the intercept of the graph of the median Karl Fischer titrator reading versus the water standard concentration in units of g H_2O/100 mL. Using this slope and intercept, any reading from the titrator can be converted to a water concentration (g H_2O/100 mL) by the following equation:

$$\text{Water Concentration} = \frac{\text{Karl Fischer Reading} - \text{Calibration Intercept}}{\text{Calibration Slope}}$$

2. Calculate the weight of bitumen and water in the sample:

   a. Volume of extract solution

$$V = \frac{V_s}{1 - 1.02C - 0.98D}$$

(See comments b and c)

   b. Grams of bitumen in the sample

$$A = C \times V$$

   c. Grams of water in the sample

$$B = D \times V$$

where: $V_s = \frac{\text{Weight of Solvent Blend (g)}}{\text{Density of Solvent Blend (kg/L)}}$

$= \text{mL of solvent blend added}$

$C = \frac{\text{Weight of Bitumen on Filter (g)}}{5.0 \times \text{Pipet Factor}}$

$= \text{g of bitumen/mL of solution}$

$D = \left(\frac{\text{Karl Fischer Reading} - \text{Calibration Intercept}}{\text{Calibration Slope}}\right) \times 0.01$

$= \text{g of water/mL of solution}$

3. Calculate the sample assay.

$$\% \text{ Bitumen} = \frac{A}{S} \times 100$$

$$\% \text{ Water} = \frac{B}{S} \times 100$$

$$\% \text{ Solids} = \frac{\text{Weight of Solids in Filter Funnel}}{S} \times 100$$

where: S = sample weight, g

4. For reject samples, calculate the % bitumen, % water and % solids for the bulk reject material by applying a correction for the water loss during preparation and subdivision. The % water loss is obtained from Method 1.4. The composition of the bulk reject sample is then given by:

$$\% \text{ Bitumen} = (\% \text{ Bitumen in Sample Analyzed}) \left(\frac{100 - L}{100}\right)$$

$$\% \text{ Water} = (\% \text{ Water in Sample Analyzed}) \left(\frac{100 - L}{100}\right) + L$$

$$\% \text{ Solids} = (\% \text{ Solids in Sample Analyzed}) \left(\frac{100 - L}{100}\right)$$

where: L = weight % water loss as determined by Method 1.4

Precision: Precision estimates for an oil sand analysis determined on 12 subsamples prepared as outlined in Method 1.2 are shown below. The variabilities indicated for the components of this average grade oil sand sample include contributory error due to subsampling. Precision of reject analysis have not been determined.

	Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
Bitumen	11.03	±0.26	2.36%
Water	4.46	±0.15	3.36%
Solids	84.51	±0.30	0.35%

Comments:

a. If a fiber tipped pen is used to number the filters, allow at least 15 minutes between numbering and weighing.

b. 1.02 is a volume correction factor for the dissolution of bitumen in the solvent blend.

c. 0.98 is a volume correction factor for the dissolution of water in the solvent blend

Determination of Bitumen, Water and Solids Content of Froth (Classical)

Scope: This method determines the bitumen, water and solids content of primary and secondary froth.

Summary: The sample is separated into bitumen, water and solids by refluxing with toluene in a solids extraction apparatus. Condensed solvent and co-distilled water are continuously separated in a trap, the water being retained in the graduated section. The solvent recycles through the extraction thimble of the extraction apparatus to dissolve the bitumen. The resulting bitumen/solvent and non-filtered solids fractions are separated by centrifuging. The solids are determined gravimetrically by combining the contributions for solids retained by the extraction thimble and for the non-filtered solids. The bitumen content of the sample is determined by difference.

Safety Considerations:

1. Isopropyl alcohol — irritant to the skin and respiratory tract. Highly flammable.
2. Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.

Apparatus, Reagents, Materials:

1. Condenser — a straight tube condenser having a water jacket at least 400 mm long. West type condenser with 24/40 standard taper joint as specified in ASTM E 123 is suitable.
2. Water trap — the trap having 24/40 standard taper joints shall be of 25 mL capacity. The design is taken from ASTM E 123. The scale divisions from 0 to 1 mL are 0.1 mL with a maximum scale error of 0.05 mL. From 1 to 25 mL, scale divisions are 0.2 mL with a maximum scale error of 0.1 mL.
3. Kettle — a heat-resistant glass vessel having a nominal capacity of 500 mL. The neck shall be a minimum of 250 mm long, including a 55/50 standard taper female joint to accommodate a kettle-to-trap adapter.
4. Kettle-to-trap adapter — the lower part of the adapter has a 55/50 standard taper male joint with a perforated downcomer extending below the ground glass surface. The upper part of the adapter is fitted with a 24/40 standard taper female joint.
5. Extraction thimble — Whatman 43 x 123 mm cellulose thimble, single thickness.
6. Thimble basket — a corrosion-resistant basket to support the thimble. See Figure 1. Fabrication from 1.5 mm diameter nichrome or chromel wire using a silver solder bottom joint is suitable.
7. Solvent distributor — a corrosion-resistant screen to snugly fit over the open end of the thimble.
8. Heating mantle — 250 W, to accommodate 500 mL kettle.

The assembled extraction apparatus is shown schematically in Figure 2.

9. Kimwipes — Type 900-S.
10. Weighing bottles — short form, 50 x 140 mm of borosilicate glass, with 55/12 ground glass rim.
11. Centrifuge — 87 rev/s max, 4275 x G, 6 x 1000 mL capacity, complying with Class 1 Group D explosion-proof requirements, equipped with an eight place horizontal head, trunion rings and shields.
12. Centrifuge tubes — 100 mL, conical, graduated as described in ASTM D 96.
13. Volumetric flasks — 250 mL, Class A.
14. Top loading balance to ± 0.001 g, 320 g capacity.
15. Drying oven — forced draft, set at 120°C.

16. Desiccator.
17. Reagents:
    Isopropyl alcohol, A.C.S. reagent grade
    Toluene, A.C.S. reagent grade.

Procedure: Sample Handling

1. Sample sizes should range from 40 to 50 g.
2. Prior to use, insert 3 rolled Kimwipes into each of a quantity of new thimbles. Place each thimble in a weighing bottle and dry, uncapped, for 1 hour at 120°C. Cap the weighing bottles and store in a desiccator until needed.
3. Weigh the weighing bottles plus thimbles to the nearest 0.001 g. Remove the Kimwipes and place the thimble in its support basket. Mount the thimble and basket in the neck of the kettle by spreading the basket's attaching wires. Clean the outside of the sample container and weigh to the nearest 0.01 g. Transfer the sample to the thimble, wash with toluene until clean and wipe dry with the Kimwipes. Place the Kimwipes in the thimble. Weigh the empty sample container.
4. Fill the kettle with toluene to a final volume of approximately 200 mL. Cover the thimble with the solvent distributor and attach the basket to the adapter. Assemble the apparatus as shown in Figure 2, ensuring all connections are vapour tight. Do not use grease on the ground glass joints.

Extraction

5. Apply heat and adjust to maintain the reflux rate such that liquid does not overflow the thimble. Continue refluxing for 30 minutes after no water is visible in any part of the apparatus except the trap, and the solvent dropping from the thimble is colorless. Discontinue heating and when refluxing has stopped, add three drops of isopropyl alcohol around the inside rim of the condenser to bring water droplets adhering to the glass surface of the condenser down into the trap.

Water

6. Allow the trap and contents to cool to room temperature. Estimate the volume of water in the trap to the nearest 0.05 mL.

Solids

7. Disassemble the apparatus, remove the thimble from its support and return it to its original weighing bottle. Dry uncapped for 3 hours at 120°C. Cool the capped assembly in a desiccator and weigh to the nearest 0.001 g.

Non-filtered Solids

8. Transfer the bitumen/solvent solution and non-filtered solids remaining in the kettle to a 250 mL flask, rinsing with small portions of toluene. Dilute to volume when cool. Invert the flask several times to suspend the fines and immediately transfer 75 mL to a clean centrifuge tube preweighed to the nearest 0.001 g. Centrifuge at 33 rev/s for 20 minutes. Decant and discard the bitumen/solvent solution. Rinse the inner walls of the tube with toluene, being careful not to dislodge any particles, and place in an oven maintained at 120°C for 1 hour. Cool in a desiccator and weigh.

Calculations: The bitumen, water and solids contents of the sample are given by:

$$\% \text{ Water} = \frac{V}{W} \times 100$$

$$\% \text{ Solids} = \frac{S + 3.33A}{W} \times 100$$

$$\% \text{ Bitumen} = 100 - (\text{wt } \% \text{ Solids} + \text{wt } \% \text{ Water})$$

where: V = volume of water retained in trap, mL. The density of water is assumed to be 1.0 kg/L.
W = weight of sample, g
S = weight of solids recovered in thimble, g
A = weight of fines recovered in centrifuge tube, g

Precision: The precision of typical froth analyses, assuming strict adherence to the procedure outlined, is indicated below. Evaluations were conducted on 15 or more replicate subsamples obtained in accordance with Method 1.6 and hence the data shown incorporates errors due to sampling.

	Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
Primary Froth			
Bitumen	68.41	±0.43	0.63%
Water	27.56	±0.38	1.38%
Solids	4.03	±0.18	4.47%
Secondary Froth			
Bitumen	25.66	±0.97	3.78%
Water	63.08	±0.65	1.03%
Solids	11.26	±0.35	3.11%

The agreement among replicate samples of secondary froth when prepared by Method 1.5 is shown below for 12 subsamples.

	Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
Bitumen	25.62	±1.17	4.57%
Water	55.16	±0.74	1.34%
Solids	19.22	±0.45	2.34%

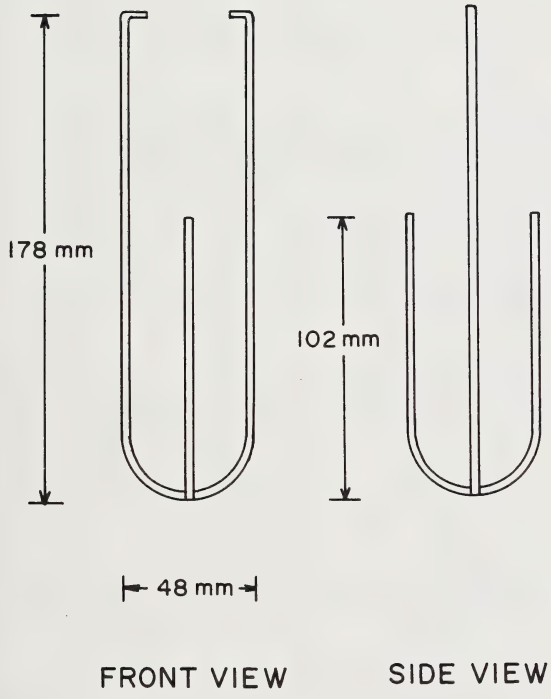


FIGURE 1: EXTRACTION THIMBLE BASKET

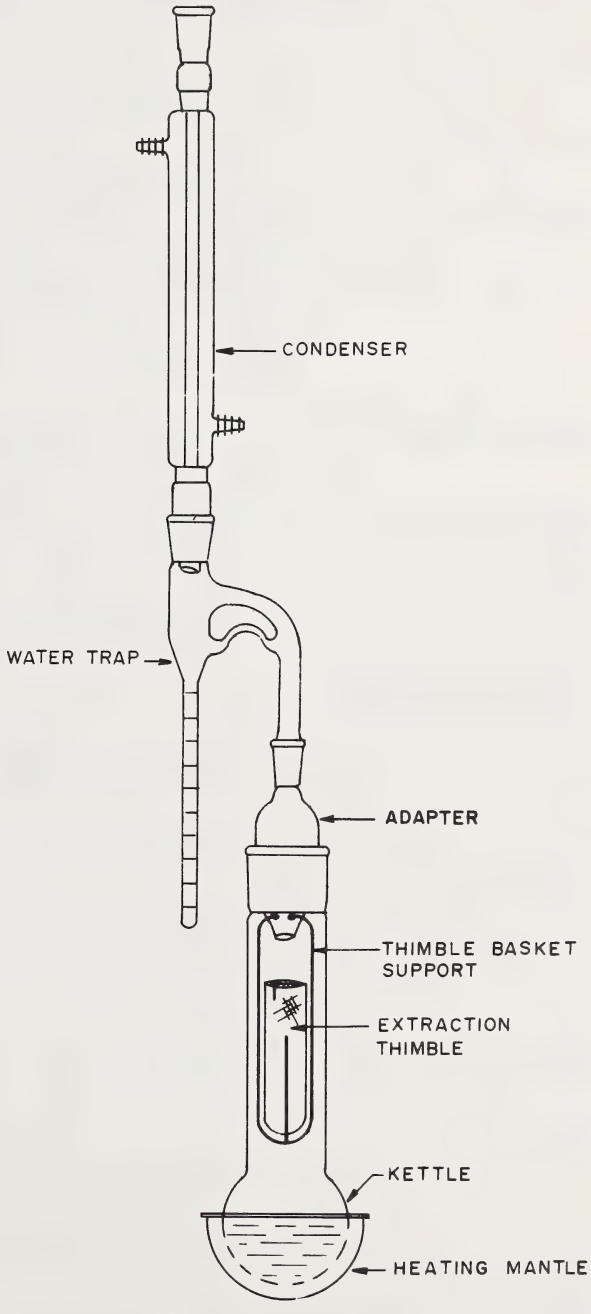


FIGURE 2: EXTRACTION APPARATUS

Syncrude Method For the Determination of Bitumen, Water and Solids Content of Froth

Scope: This method determines bitumen, water and solids content of primary and secondary froth. The method is limited to samples between 15 and 30 g.

Summary: The bitumen and water in the sample are extracted from the froth by shaking the sample with a known quantity of solvent. The solvent, a 74% toluene / 26% isopropyl alcohol blend, dissolves both the bitumen and water in the sample. An aliquot of this extract is evaporated to remove the solvent and water, and the bitumen is determined gravimetrically. Another aliquot of the extract is analyzed for water content by an automatic Karl Fischer titration. If the water dissolution capacity of the solvent blend is exceeded, isopropyl alcohol is added to the sample-solvent mixture, the extraction is continued, and a second Karl Fischer titration is performed. Solids are can be determined by difference or can be filtered, dried, and weighed for a mass balance check.

Safety Considerations:

1. Dimethyldichlorosilane — evolves toxic and corrosive fumes of hydrogen chloride upon contact with moisture. Avoid contact with skin, eyes, or clothing; do not breath fumes. Neutralize excess reagent by cautious addition of methanol.
2. Isopropyl alcohol — irritant to the skin and respiratory tract. Highly flammable.
3. Karl Fischer reagent — toxic by skin absorption and inhalation. Flammable.
4. Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.

Apparatus, Reagents, Materials: Extraction, Bitumen Determination, Water Determination.

1. Nalgene linear polyethylene bottles — 1000 mL capacity with polypropylene screw closures. Nalge 2104.
2. Reciprocating shaker — 40 mm stroke, set at approximately 5 cycles/s, and equipped with carrier.
3. Syringe — 10 mL, glass, Luer - Lok tip.
4. Disposable filter assemblies — Millipore Millex filters, 0.45 μm, 25 mm diameter, catalogue no. SLHA 025 OS.
5. Erlenmeyer flasks — 25 mL, with ground glass tops fitted with ground glass stoppers.
6. Transfer pipets — 5 and 20 mL, Class A, with bulbs.
7. Glass fiber filters — 150 mm diameter. Reeve Angel grade 934 AH.
8. Petri dishes — 100 mm diameter, 10 mm height.
9. Drying rack — a horizontal rod suspended between two retort stands which are approximately 1 m apart. Ten 20 mm foldback clips are hung on the rod.
10. Photovolt Aquatest II Automatic Karl Fischer Titrator and accompanying vessel and generator solutions. Photovolt Corporation, 1115 Broadway, New York, NY 10010.
11. Push button adjustable syringe — 200 μL. Hamilton CR700-200.
12. Densimeter — readable to ±0.0001 kg/L. Method 3.6 describes the use of a suitable densimeter.
13. Balances:
    Top loading balance to ±0.01 g, 1200 g capacity.
    Analytical balance.
14. Drying oven — forced draft, set at 110°C.

15. Desiccator.
16. Reagents:
    Isopropyl alcohol, 99 mol %.
    Toluene, A.C.S. reagent grade.
17. Molecular sieves — type 4A.

Optional Solids Determination

1. Filtering funnel — Buchner type with fine fritted disc, 350 mL capacity. Corning 36060.
2. Filtering flask — Erlenmeyer with side arm, heavy walls, 2000 mL capacity. Corning 3560.
3. Vacuum pump and tubing — 8.3 L/s free air capacity.
4. Reagents:
    Acetone, A.C.S. reagent grade.
    Filter aid, Celite 499.

Preparation of Water Standards

1. Six serum bottles — 125 mL, with Viton flange type stoppers and aluminum seals.
2. Six volumetric flasks — 100 mL, Class A.
3. Reagents:
    Dimethyldichlorosilane (DMDCS)
    Methanol, A.C.S. reagent grade, dry.
4. Distilled water.

Preparation Steps: Solvent Blend Preparation

1. Fill a large closed container with 74% toluene and 26% isopropyl alcohol (volume %).
2. Add molecular sieves, type 4A, to the container and allow the solvent blend to dry for 24 hours. If the weather is unusually humid a longer drying time is required. Absolutely dry solvent (no reading on a Karl Fischer titrator) should be used to prepare the water standards so that their absolute water content will be known. However, a small residual water content (35 μg in a 100 μL injection into the Karl Fischer titrator) can be tolerated for sample analysis as long as this solvent blank value is known and is subtracted from the sample water reading.
3. Determine the density of the blend (Method 3.6). A 74% toluene / 26% isopropyl alcohol mixture has a density of 0.8440 kg/L at 20°C. If the density falls outside the range of 0.8435 to 0.8445 kg/L adjust the solvent blend as follows:
    i) For densities greater than the permitted range, add isopropyl alcohol until the correct density is obtained.
    ii) For densities less than the permitted range, add toluene until the correct density is obtained.

Preparation of Dry Isopropyl Alcohol (IPA)

4. Fill a large closed container with isopropyl alcohol and add molecular sieves, type 4A. Allow the isopropyl alcohol to dry 24 hours. Absolutely dry isopropyl alcohol (no reading on the Karl Fischer titrator) must be obtained.

Preparation of Water Standards

5. All glassware used is first treated with the silylating agent DMDCS to prevent adsorption of water on the glassware for the standard solutions.
    i) Clean volumetric flasks and serum bottles with a strong detergent. Rinse well with water and then with acetone. Dry in oven and desiccate until cool.

ii) Immerse glassware in a 5-10% DMDCS solution (in toluene) for a few minutes. Rinse glassware with dry methanol, dry in oven and desiccate until cool. Keep glassware stoppered with stoppers or septa which have also been dried in a desiccator. Hydrogen chloride is liberated from DMDCS on contact with moisture, therefore work in a fumehood and use gloves. Any DMDCS spills are easily neutralized with methanol.

6. Prepare six standard water solutions by weighing distilled water (to the nearest 0.0001 g) into 100 mL volumetric flasks. The solutions should contain approximately 0.25, 0.50, 0.80, 1.20, 1.60, and 2.00 g of water respectively. Use the dry 74% toluene / 26% isopropyl alcohol blend as the solvent for these standard solutions. Mix the solutions well and transfer them to the prepared serum bottles. Immediately stopper and seal the bottles. These solutions should keep for several months.

Calibration of the Karl Fischer Titrator

7. The Aquatest II Karl Fischer titrator and syringe should be calibrated daily. Adjust the syringe so that it delivers a volume of about 100 μL. Do not change this volume between running the standard and sample solutions on the titrator.

8. Rinse the syringe three times with the most dilute water standard. Allow a few minutes to ensure that the chamber of the syringe is at its equilibrium volume, fill the syringe and inject an aliquot into the titration cell of the instrument. Flip the switch to TITRATE and record the number displayed when the END light comes on. Zero the display on the titrator, refill the syringe with the same standard solution, inject this aliquot into the titration cell and record the reading from the titrator. Titrate a third aliquot of the standard solution in the same manner. Then repeat this entire procedure for each successive standard solution. Determine the median titration value for each water standard. If the water readings for the 0.80 g of water standard vary by more than 15 μg, check instrument and syringe performance.

Pipet Calibration

9. Calibrate a 5 mL transfer pipet with a solution of bitumen and water in the solvent blend which approximates the extract obtained in this method. Use only this pipet for the determination of bitumen. Calculate the pipet factor:

$$\frac{\text{volume of mixture delivered by 5 mL pipet}}{5.0}$$

where the volume of the mixture delivered is determined from the weight and density (Method 3.6).

Procedure:

1. Measure the density of the solvent blend daily. The permitted range is 0.8435 to 0.8445 kg/L. Inject 100 μL of the solvent blend into the Karl Fischer titrator. Any reading greater than zero must be subtracted from subsequent sample readings.

2. Measure the density of the dried isopropyl alcohol daily. Using the Karl Fischer titrator verify that the isopropyl alcohol is dry.

3. Weigh the Nalgene bottle containing the sample to the nearest 0.01 g. If the sample is received in a container other than a Nalgene bottle, proceed as follows:

   i) Weigh a Nalgene bottle containing 3 Kimwipes to the nearest 0.01 g. If the optional solids determination is to be performed, the weight of the bottle and Kimwipes must be determined separately.

   ii) Weigh the sample jar containing the sample to the nearest 0.01 g.

   iii) Remove the Kimwipes from the Nalgene bottle, transfer the sample, and then clean out the sample jar with the preweighed Kimwipes. All Kimwipes must be returned to the Nalgene bottle.

   iv) Weigh the empty sample jar to the nearest 0.01 g.

4. Add solvent blend to the Nalgene bottle. For primary froth samples add approximately 500 mL of solvent blend. For secondary froth samples add a volume of solvent blend according to the following table:

Sample Size (g)	Minimum Volume of Solvent Required (mL)
20 or less	500
25	600
30	700

If solvent blend was used to transfer the sample to the Nalgene bottle, then the volume of solvent added must be adjusted to take this volume into account.

Tightly cap the bottle and record its weight to the nearest 0.01 g.

Extraction

5. Place the Nalgene bottle containing the sample and solvent blend on its side on the reciprocating shaker. Allow the mixture to shake for 60 minutes. This extraction time is not critical as long as it is greater than 45 minutes.

Water Determination

6. Remove the Nalgene bottle from the shaker and allow the sample to settle for one minute. Transfer a 20 mL aliquot of the extract solution to a 25 mL Erlenmeyer flask. Do not remove more than 20 mL from the extract solution. Stopper the flask and replace the cap on the Nalgene bottle. Titrate the extract in the Erlenmeyer flask as soon as possible after it has been removed from the Nalgene bottle. Rinse the Hamilton syringe three times with the sample extract solution from the Erlenmeyer flask. As in the calibration procedure allow a few minutes before filling the syringe with the aliquot to be titrated. Refill the syringe and inject this aliquot into the titrator. Flip the titrator switch to TITRATE. When the END light comes on record the value of the aliquot titer. If this value is 2100 μg or greater, an extra step (#7) is required to ensure that the water dissolution is complete at this point. Save the remaining extract in the Erlenmeyer flask for the bitumen determination.

   To minimize evaporation of the extract and therefore reduce the error in the bitumen determination keep the Erlenmeyer flask stoppered whenever possible.

7. If the initial water determination exceeds 2100 μg on the Karl Fischer titrator, tare the Nalgene bottle containing the remaining sample-solvent mixture and add approximately 100 mL of dried isopropyl alcohol to the bottle. Record its weight to the nearest 0.01 g. Place the Nalgene bottle on the shaker and allow it to shake for about five minutes. Rinse the Hamilton syringe three times with the sample extract solution. As in the calibration procedure, allow a few minutes before filling the syringe with the aliquot to be titrated. Then shake the sample extract a few times by hand, allow a minute for the coarse solids to settle, fill the syringe, and inject this aliquot into the titrator. Flip the titrator switch to TITRATE. When the END light comes on record the value of the aliquot titer as the second water reading.

Bitumen Determination

8. Dry the glass fiber filters by placing an open box of filters in an oven at 110°C for 1 hour. Cool them in a desiccator. Number the filters and weigh to the nearest 0.0001 g. (a)

9. Rinse a 10 mL syringe with the sample extract retained in step 6. Withdraw approximately 7 mL of the extract and attach a 0.45 μm Millipore Millex filter assembly to the 10 mL syringe. Filter the extract into another 25 mL Erlenmeyer flask. Stopper the flask if the solution aliquot is not to be taken immediately. Rinse the 5 mL transfer pipet with the extract solution. Support a weighed glass fiber filter on a Petri dish. Pipet a 5 mL aliquot of the solution onto the filter by continuously moving the pipet to disperse the extract evenly on the filter surface. Hang the filter from the drying rack to evaporate the solvent. The time required to dry the filter is critical and is selected using a 74% toluene/26% isopropyl alochol solution of known bitumen concentration. Five mL aliquots are applied to filters and these are weighed at varying times. The time which gives the correct bitumen weight is selected for sample analysis. This drying time is approximately 15 minutes and need only be determined for the particular laboratory conditions in use. Weigh the filter with the bitumen.

10. If the optional solids determination is to be performed proceed to step 11. If the solids are to be determined by difference and the sample was received in the Nalgene bottle, clean and dry the bottle at 110°C for 30 minutes. When cool weigh to the nearest 0.01 g.

Optional Solids Determination

11. Fill the filtering funnel with enough Celite 499 to make a loosely packed layer approximately 30 mm thick, covering the entire surface of the glass frit. Weigh the funnel plus Celite 499 to the nearest 0.01 g.
12. Set up the filtering funnel and flask and attach to the vacuum outlet. Slurry the Celite 499 with toluene. Turn on the vacuum and decant the sample extract from the Nalgene bottle into the funnel. When most of the extract has filtered through, pour any remaining extract and solids into the funnel.
13. Wash the inside of the Nalgene bottle with solvent blend and pour the washings into the filter funnel to clean the solids. Gently pass air into the Nalgene bottle to dry it out. Then tap any remaining solids into the filter funnel. If the sample was received in the Nalgene bottle, weigh to the nearest 0.01 g after drying at 110°C for 30 minutes.
14. Wash the solids in the funnel with several portions of solvent blend until all the bitumen has been removed (effluent appears clear). Then wash the clean solids with acetone to aid in drying. Leave the vacuum on for 3 or 4 minutes to remove most of the acetone from the solids.
15. Place the filtering funnel containing the solids in the oven (110°C) for approximately 45 minutes to ensure complete drying, allow to cool, then weigh. If Kimwipes are present in the bottle, do not attempt to separate these from the funnel. Wash and dry them with the solids. Subtract the weight of the Kimwipes (determined in step 3) from the weight of the material in the funnel to obtain the weight of the solids.

Calculations:

1. The Karl Fischer titrator calibration data is subjected to a linear least squares regression to obtain the slope and the intercept of the graph of the median Karl Fischer titrator reading versus the water standard concentration in units of g H_2O/100 mL. Using this slope and this intercept, any reading from the titrator can be converted to a water concentration (H_2O/100 mL) by the following equation:

$$\text{Water Concentration} = \frac{\text{Karl Fischer Reading} - \text{Calibration Intercept}}{\text{Calibration Slope}}$$

2. Calculate the weight of bitumen and water in the sample.

i) When no extra isopropyl alcohol has been added:

a) Volume of extract solution

$$V = \frac{V_s}{1 - 1.02C - 0.98D}$$

(See comments b and c)

b) Grams of bitumen in the sample

$$A = C \times V$$

c) Grams of water in the sample

$$B = D \times V$$

where:

$$V_s = \frac{\text{Weight of Solvent Blend (g)}}{\text{Density of Solvent Blend (kg/L)}}$$

= mL of solvent blend added

$$C = \frac{\text{Weight of Bitumen on Filter (g)}}{5.0 \times \text{Pipet Factor}}$$

= g of bitumen/mL of solution

$$D = \frac{\text{Karl Fischer Reading} - \text{Calibration Intercept}}{\text{Calibration Slope}} \times 0.01$$

= g of water/mL of solution

ii) When extra isopropyl alcohol has been added:

a) Volume of extract solution before the addition of extra isopropyl alcohol

$$V = \frac{V_s}{1 - 1.02C - 0.98D}$$

b) Grams of bitumen in the sample

$$A = C \times V$$

c) Grams of water in the sample

$$B = 20D + \frac{E\,[(1 - 0.98D)\,V + V_{IPA} - 20 + 19.60D]}{1 - 0.98E}$$

where:

$$V_s = \frac{\text{Weight of Solvent Blend Added (g)}}{\text{Density of Solvent Blend (kg/L)}}$$

= mL of solvent blend added

$$C = \frac{\text{Weight of Bitumen on Filter (g)}}{5.0 \times \text{Pipet Factor}}$$

= g of bitumen/mL of solution

$$D = \frac{\text{First Karl Fischer Reading} - \text{Calibration Intercept}}{\text{Calibration Slope}} \times 0.01$$

= g of water/mL of initial solution (before IPA was added)

$$E = \frac{\text{Second Karl Fischer Reading} - \text{Calibration Intercept}}{\text{Calibration Slope}} \times 0.01$$

= g of water/mL of final solution (after IPA was added)

$$V_{IPA} = \frac{\text{Weight of IPA Added (g)}}{\text{Density of IPA (kg/L)}}$$

3. Calculate the sample assay.

$$\% \text{ Bitumen} = \frac{A}{S} \times 100$$

$$\% \text{ Water} = \frac{B}{S} \times 100$$

$$\% \text{ Solids} = 100 - (\text{wt \% Bitumen} + \text{wt \% Water})$$

where: S = sample weight, g

4. If solids were measured by the optional gravimetric procedure then:

$$\% \text{ Solids} = \frac{\text{Weight of Solids in Filter Funnel}}{S} \times 100$$

Precision: Typical precision values for froth analyses conducted in the manner described are tabulated below. Estimates were determined from 12 or more samples collected in rapid succession from pilot plant process streams and hence incorporate sampling variability.

	Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
Primary Froth			
Bitumen	64.49	±0.51	0.80%
Water	27.34	±0.51	1.88%
Solids	8.18	±0.25	3.03%
Secondary Froth			
Bitumen	40.81	±0.73	1.78%
Water	48.14	±0.66	1.37%
Solids	11.05	±0.86	7.82%

The % Solids were determined by difference.

Comments:

a. If a fiber tipped pen is used to number the filters, allow at least 15 minutes between numbering and weighing.

b. 1.02 is a volume correction factor for the dissolution of bitumen in the solvent blend.

c. 0.98 is a volume correction factor for the dissolution of water in the solvent blend.

Determination of Bitumen, Water and Solids Content of Middlings and Tailings Samples (Classical)

Scope: This method determines the bitumen, water and solids content of middlings and tailings samples. Preferred sample sizes range from 250 to 600 g, although the method may be modified for smaller samples.

Summary: The sample is separated into bitumen, water and solids by refluxing with toluene in a solids extraction apparatus. Condensed solvent and co-distilled water are continuously separated in a trap. The water is drained from the lower portion of the trap while the solvent recycles through the extraction thimble to dissolve bitumen. When the extraction is complete, the clean solids retained in the thimble are dried and weighed. A density measurement is employed to determine the bitumen content of the extract. Water is determined by difference.

Safety Considerations:

1. Hydrochloric acid — highly toxic by inhalation. A strong irritant to eyes and skin.
2. Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.

Apparatus, Reagents, Materials:

1. Condenser — an indented tube condenser having a water jacket at least 535 mm long with a 29/42 standard taper male joint at the base.
2. Water trap — constructed to continuously separate water and solvent. The trap portion, which is approximately 25 mm in diameter and 220 mm long, has a volume of about 130 mL. The lower end is fitted with a stopcock for removal of water while the upper section has a 29/42 standard taper female joint to accommodate the condenser. The downcomer has a 103/60 standard taper male joint for connection to the kettle and is perforated with 3 mm diameter holes below the ground glass.
3. Kettle — a heat-resistant glass vessel having a capacity of 2000 mL. The neck has a minimum length of 390 mm and includes a 103/60 standard taper female joint.
4. Extraction thimble — Whatman 85 x 200 mm cellulose thimble, single thickness.
5. Thimble basket — a corrosion-resistant basket to support the thimble. See Figure 1. Fabrication from 3 mm diameter nichrome wire using a silver solder bottom joint is suitable.
6. Solvent distributor — corrosion-resistant, as shown in Figure 2.
7. Heating mantle — 500 W, to accommodate 2000 mL kettle.

The assembled extraction apparatus is shown schematically in Figure 3. If samples are less than 100 g, then the extraction apparatus described in Method 2.7 is used with the exception that the lower end of the water trap is fitted with a drain cock. Volumes employed in the following procedure are then gauged accordingly.

8. Kimwipes — Type 1300.
9. Supply of 800 mL beakers.
10. Volumetric flasks — 250 and 1000 mL, Class A.
11. Syringe — 5 mL, glass, Luer-Lok tip.
12. Disposable filter assemblies — Millipore Millex filters, 0.45 μm, 25 mm diameter, catalogue no. SLHA 025 OS.
13. Densimeter — six place densimeter with constant temperature water bath for temperature control to ±0.01°C. The water bath is operated at 20°C.
14. Balances:
    Top loading balance to ±0.01 g, 1200 g capacity.
    Analytical balance.

15. Drying oven — forced draft, set at 120°C.
16. Desiccator.
17. Reagents:
    Hydrochloric acid, A.C.S. reagent grade.
    Toluene, A.C.S. reagent grade.
18. Distilled water.

Procedure: Sample Handling

1. Insert 3 Kimwipes into each of a quantity of thimbles. Place the thimbles into 800 mL beakers and weigh to the nearest 0.01 g.
2. Clean the outer walls of the sample container and lid. Weigh to the nearest 0.1 g. Carefully add 0.5 mL of concentrated hydrochloric acid to the sample. Then add approximately 100 mL of toluene and stir until all the bitumen adhering to the wall of the sample container is dissolved.
3. Remove the Kimwipes from the thimble, insert the thimble into a thimble basket and mount the basket by its support into the neck of a kettle. Add approximately 900 mL of toluene to the kettle by pouring it through the thimble.
4. Restir the sample and while it is still in motion transfer to the thimble. Wash the container with toluene to remove all the bitumen. Add the washings to the thimble. Transfer the bulk of the remaining solids by scraping with a spatula. Finally, rinse and transfer remaining solids with distilled water. Clean and dry the container and lid with the Kimwipes and place them in the thimble. Weigh the container and lid.

Extraction

5. Assemble the extraction apparatus as shown in Figure 3, ensure all joints are vapour tight, and begin refluxing. Drain and discard water from the trap when it nears the trap overflow. The extraction is complete when the level of water in the trap is constant and solvent dripping from the thimble is clear. Terminate the extraction and allow the apparatus to cool.

Calibration of Densimeter

6. Prepare a series of standard solutions of middlings and tailings bitumen in toluene covering the range 0.3 - 12 g/250 mL. (a)
7. Filter the standards through a 0.45 μm filter and determine the density of the solutions to six places.
8. Prepare a calibration curve by plotting the density of the standards versus the bitumen concentration in grams of bitumen per 250 mL. Calculate the slope and intercept of the plot using a linear least square regression. Coefficients of determination better than 0.999 are expected. The calibration does not have to be repeated daily, but several points on the calibration curve should be checked periodically to confirm the calibration.

Bitumen Determination

9. Disassemble the extraction apparatus and pour the bitumen/toluene extract into a 1000 mL volumetric flask and dilute to volume with toluene. Filter several milliliters of the solution through a 0.45 μm filter and determine its density to six decimal places. Ensure that the measured density falls within the range of the calibration.

Solids Determination

10. Remove the thimble from the extraction apparatus, place it in its beaker and dry for 12 hours at 120°C. Cool and reweigh.

Calculations: The bitumen, water and solids contents of the sample are given by:

$$\% \text{ Bitumen} = \frac{B}{W} \times 100$$

$$\% \text{ Solids} = \frac{S}{W} \times 100$$

$$\% \text{ Water} = 100 - (\text{wt \% Bitumen} + \text{wt \% Solids})$$

where: W = weight of sample, g

S = weight of solids recovered in thimble, g

$$B = \frac{\text{Sample Density} - \text{Calibration Intercept}}{\text{Calibration Slope}} \times 4$$

= weight of bitumen in sample, g

Precision: Data tabulated below indicates typical precision values associated with the bitumen, water and solids analysis of middlings and tailings samples. Estimates reflecting the repeatability of a middlings analysis were determined on 37 replicate subsamples prepared by Method 1.6 and analyzed using the small extractor assemblies. Precision values for primary and secondary tailings were evaluated from 10 replicate samples obtained in rapid succession from pilot plant process streams and analyzed using large extractor assemblies. All data includes errors due to sampling.

	Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
Middlings			
Bitumen	7.32	±0.15	2.05%
Water	75.91	±0.42	0.55%
Solids	16.77	±0.38	2.27%
Primary Tailings			
Bitumen	0.87	±0.06	6.90%
Water	35.01	±1.47	4.20%
Solids	64.12	±1.48	2.31%
Secondary Tailings			
Bitumen	0.44	±0.02	4.55%
Water	79.98	±1.71	2.14%
Solids	19.58	±1.71	8.73%

Comments:

a. The bitumen for the standard solutions is prepared by extracting a large number of middlings and tailings samples on a solids extraction apparatus, removing non-filtered solids by centrifuging, removing toluene by evaporation, and determining the residual toluene content by the procedure described in Method 2.7.

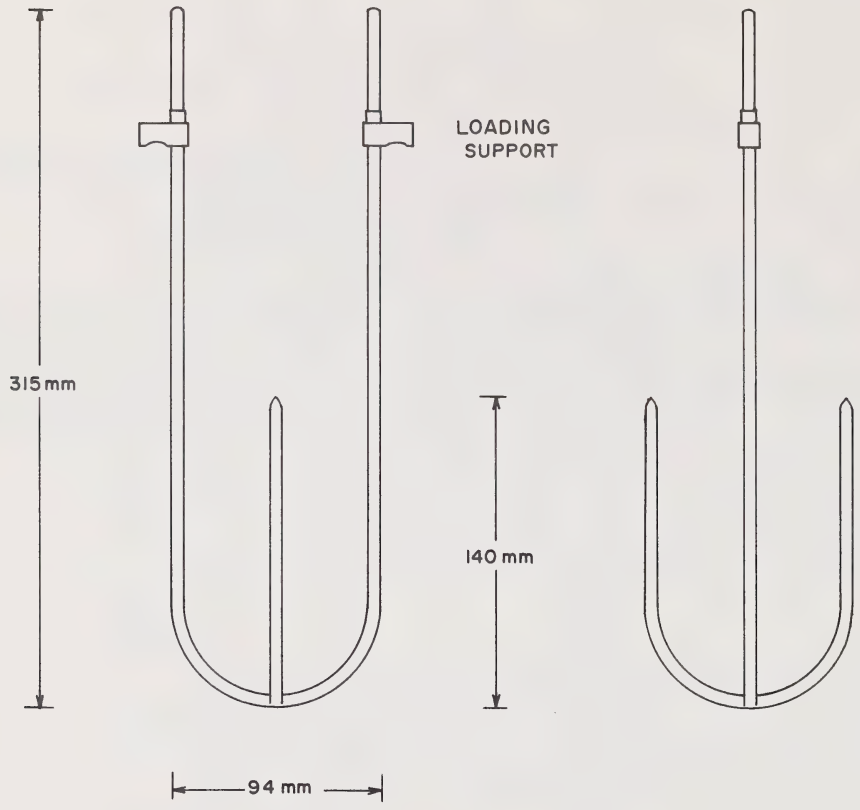


FIGURE 1: EXTRACTION THIMBLE BASKET

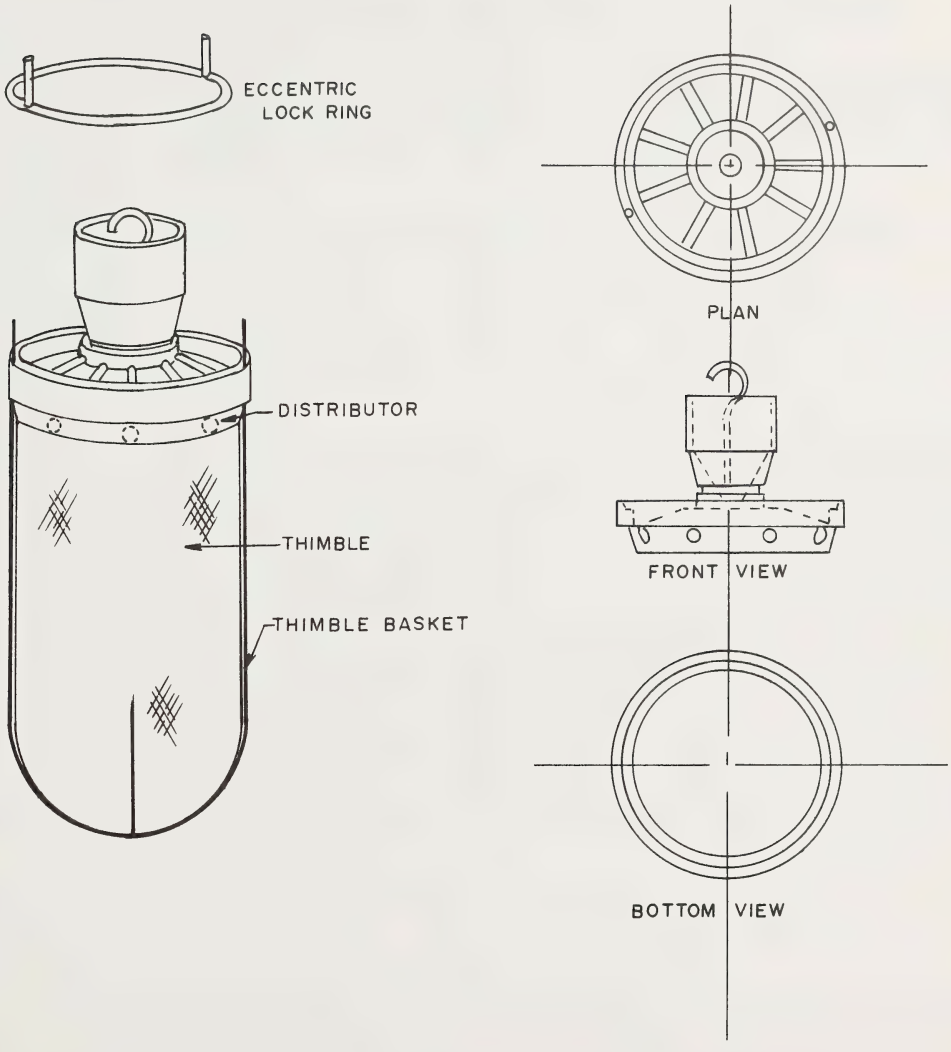


FIGURE 2: THIMBLE ASSEMBLY AND SOLVENT DISTRIBUTOR

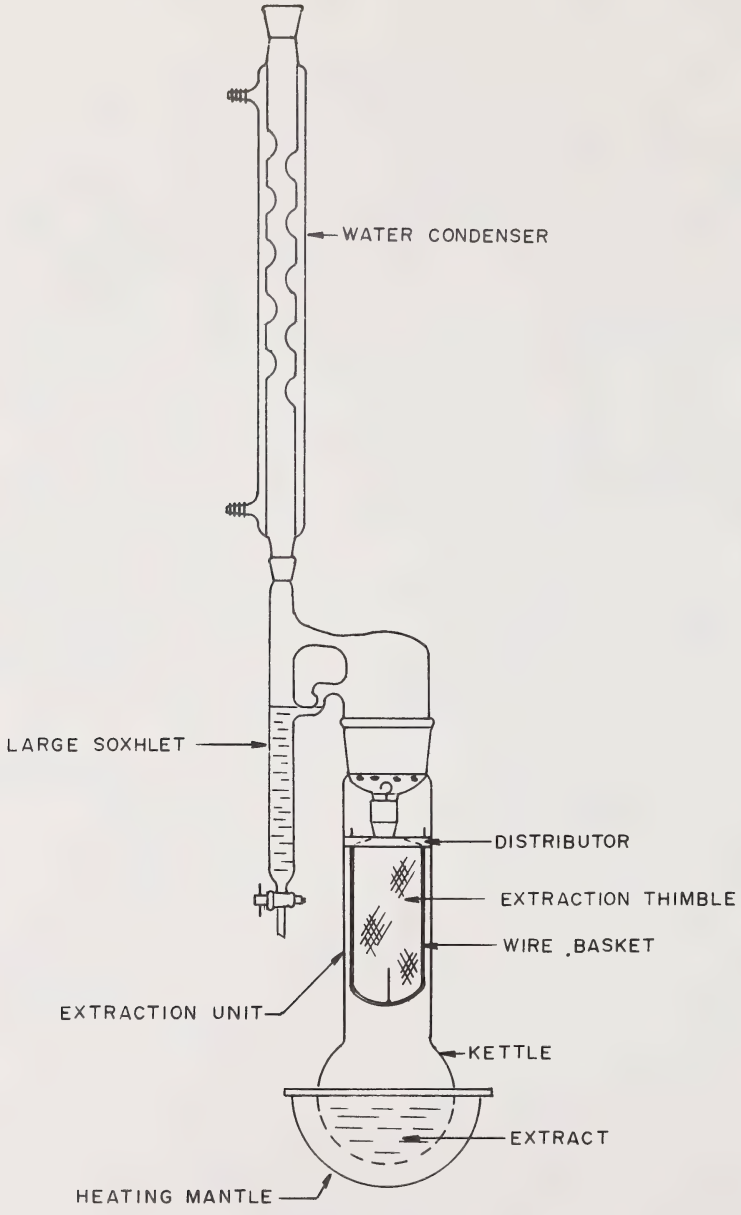


FIGURE 3: EXTRACTION APPARATUS

Syncrude Method For the Determination of Bitumen, Water and Solids Content of Middlings and Tailings Samples

Scope: This method determines the bitumen, water and solids content of middlings, primary tailings and secondary tailings samples of approximately 50 grams.

Summary: The bitumen in the sample is extracted by shaking it with 1,1,1-trichloroethane, which dissolves only the bitumen. The organic phase is separated from the water and solids by using phase separating paper. The bitumen in the 1,1,1-trichloroethane extract is determined gravimetrically. The solids are dried and weighed. Water is reported by difference.

Safety Considerations: 1,1,1-Trichloroethane — moderately toxic by skin absorption and inhalation. Contains inhibitor to prevent formation of phosgene on exposure to heat.

Apparatus, Reagents, Materials:

1. Nalgene linear polyethylene bottles — 250 mL capacity with polypropylene screw closures. Nalge 2104.
2. Reciprocating shaker — 40 mm stroke, set at 3 cycles/s, and equipped with carrier.
3. Centrifuge — 87 rev/s max., 4275 x G, 6 x 1000 mL capacity, complying with Class 1 Group D explosion-proof requirements, equipped with a six place horizontal head and 250 mL aluminum cups.
4. Phase separating filter papers — 150 mm diameter. Schleicher and Schuell Inc., catalogue no. 595 HY.
5. Glass filter funnels — 90 mm OD, with long stems. Kimble 28950.
6. Filter funnel support and retort stand.
7. Volumetric flasks — 200 and 250 mL, Class A.
8. Syringe — 10 mL, glass, Luer-Lok tip.
9. Disposable filter assemblies — Millipore Millex filters, 0.45 μm, 25 mm diameter, catalogue no. SLHA 025 OS.
10. Erlenmeyer flasks — 25 mL, with ground glass mouths fitted with ground glass stoppers.
11. Transfer pipet — 5 mL, Class A, with bulb.
12. Glass fiber filters — 150 mm diameter. Reeve Angel grade 934 AH.
13. Petri dishes — 100 mm diameter, 10 mm height.
14. Drying rack — a horizontal rod suspended between two retort stands which are approximately 1 m apart. Ten 20 mm foldback clips are hung on the rod.
15. Disposable aluminum dishes — 140 mm diameter by 40 mm height.
16. Balances:
    Top loading balance to ±0.01 g, 1200 g capacity.
    Analytical balance.
17. 1,1,1-Trichloroethane, inhibited (Chlorothene NU, Dow Chemical of Canada Ltd.).
18. Drying oven — forced draft, set at 110°C.
19. Desiccator.

Procedure: Pipet Calibration

1. Calibrate a 5 mL transfer pipet with a 1,1,1-trichloroethane/bitumen solution which approximates the extract obtained in this method. Use only this pipet for the determination of bitumen. Calculate the pipet factor:

$$\frac{\text{volume of mixture delivered by 5 mL pipet}}{5.0}$$

where the volume of the mixture delivered is determined from the weight and density (Method 3.6).

Extraction

2. Weigh the Nalgene bottle in which the sample has been collected to nearest 0.01 g.
3. Add approximately 50 mL 1,1,1-trichloroethane to the bottle and cap tightly.
4. Place the Nalgene bottle containing sample and solvent on the reciprocating shaker for approximately 10 minutes. This time is not critical as long as it is at least 5 minutes.
5. Place bottles into centrifuge cups and balance, in pairs, to ± 1.0 g. Centrifuge for 5 minutes at 33 rev/s. This will separate the emulsion created from shaking the sample. Three phases will appear: a top layer of water and fines, a middle layer of solvent and bitumen, and a bottom layer of heavy solids and water.
6. Decant the upper two liquid phases in the bottle into a folded phase separating filter paper suspended in a glass funnel which is held over a volumetric flask. Use 200 mL volumetric flasks for secondary tailings and 250 mL volumetric flasks for middlings and primary tailings. The water and fines layer will remain in the filter while the solvent/bitumen phase will flow into the volumetric flask.
7. Wash the solids remaining in the bottle with several portions of solvent. Decant the solvent into the phase separating filter. Repeat until the solids washings are clear, then use a fine forceful stream of solvent to wash any bitumen from the filter paper. Do this until the effluent from the filter is clear. This step should require less volume than the volume required to fill the volumetric flask.

Bitumen Determination

8. Dry the glass fiber filters by placing an open box of filters in an oven at 110°C for one hour. Cool them in a desiccator. Number the filters and weigh to the nearest 0.0001 g. (a)
9. Bring the volumetric flask containing the extracted bitumen to volume with 1,1,1-trichloroethane and mix well. Rinse a 10 mL syringe with this solution. Withdraw approximately 7 mL of the solution and attach a 0.45 μm Millipore Millex filter assembly to the 10 mL syringe. Filter into a 25 mL Erlenmeyer flask. Stopper the flask if the solution aliquot is not to be taken immediately. Rinse the 5 mL transfer pipet with the extract solution. Support a weighed glass fiber filter on a Petri dish. Pipet a 5 mL aliquot of the solution onto the filter by continuously moving the pipet to disperse extract evenly on the filter surface. Hang the filter from the drying rack to evaporate the solvent. The time required to dry the filter is critical and is selected using a 1,1,1-trichloroethane solution of known bitumen concentration. Five mL aliquots are applied to filters and these are weighed at varying times. The time which gives the correct bitumen weight is selected for sample analysis. This drying time is approximately 10 minutes and need only be determined for the particular laboratory conditions in use. Weigh the filter and bitumen.

Solids Determination

10. Use 1,1,1-trichloroethane to wash the water and fines remaining in the phase separating filter paper into a weighed aluminum dish. Also transfer the solids from the Nalgene bottle into the aluminum dish. Place the dish into an oven set at 110°C for approximately 1.5 hours or until the solids are dry. Allow the solids to cool and weigh to the nearest 0.01 g.

12. Dry the empty Nalgene bottle in an oven set at 110°C, cool, and weigh to the nearest 0.01 g to determine the original bottle weight.

Calculations: The bitumen, water and solids contents of the sample are given by:

$$\% \text{ Bitumen} = \frac{B}{W} \times 100$$

$$\% \text{ Solids} = \frac{S}{W} \times 100$$

$$\% \text{ Water} = 100 - (\text{wt \% Bitumen} + \text{wt \% Solids})$$

where: W = weight of sample, g

S = weight of solids in sample, g

$$B = \frac{\text{Weight Bitumen on Filter (g)}}{5 \times \text{Pipet Factor}} \times \text{Volume of Flask (mL)}$$

= weight of bitumen in sample, g

Precision: Typical precision estimates for the analysis of a middlings sample conducted in adherence to the procedure outlined are shown below. Data was developed from a set of 8 samples taken in rapid succession from a pilot plant process stream. Variability due to sampling is hence included. An evaluation for the precision of tailings analyses has not been undertaken.

	Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
Bitumen	7.34	±0.12	1.63%
Water	66.89	±0.63	0.94%
Solids	25.77	±0.64	2.48%

The weight % water was determined by difference.

Comments: a. If a fiber tipped pen is used to number the filters, allow at least 15 minutes between numbering and weighing.

CHAPTER 3

FROTH TREATMENT PROCESS ANALYSIS

The bitumen-rich froth collected from the separation vessels of the hot water extraction process must be further treated to remove solid particles and water. The purification process consists of a diluent addition step to lighten the hydrocarbon density, two centrifuging stages to remove solids and water, and a diluent recovery step. Analytical inspection of these process streams includes analyses for bitumen, diluent, water and solids, and some physical property measurements of the hydrocarbon phase. The analyses are needed for process control and material balance calculations.

The determination of bitumen, diluent, water and solids is performed by separating the sample into the individual components using a specially-designed solids extraction apparatus. This separation technique is similar to the classical methods for bitumen, water and solids determination described in the previous chapter. The solvent/hydrocarbon solution must be further analyzed for diluent (naphtha) and bitumen content. Several techniques are described for this analysis depending upon the stream to be analyzed. In Method 3.1, analysis of feed and product streams, the bitumen content is determined spectrophotometrically and the naphtha content obtained by difference. Method 3.2, analysis of tailings, describes a spectrophotometric approach based upon absorption measurements in the visible and infrared regions to determine bitumen and naphtha. The time required for these analyses is 10 to 12 hours.

The determination of naphtha in any froth treatment process stream by gas chromatography is described in Method 3.3. Although this method determines only the naphtha component, the procedure can be completed in 30 minutes. When combined with the solids extractor methods, Method 3.3 also permits an alternative technique for completion of the bitumen, naphtha, water and solids determination. If the naphtha content is determined on a duplicate sample, Method 3.1 may be modified to determine the bitumen by difference, and Method 3.2 may be modified to determine the bitumen gravimetrically.

The water content of naphtha diluent is determined by an automated Karl Fischer titration in Method 3.4. No sample preparation is necessary. The sample is injected directly into the titration cell and the titrator gives a readout of the micrograms of water present. The time required for a single determination is approximately 8 minutes.

Physical property measurements of the hydrocarbon phase include viscosity and density. These measurements are especially suited to monitor diluent addition and recovery. Viscosity is determined using a rotational viscometer. The viscometer, when equipped with an ultra-low adapter, provides precise measurements from 0.1 to 100 mPa.s. This method requires approximately 15 minutes per measurements. Measurement of hydrocarbon density (Method 3.6) is based upon the vibration of a small U-shaped tube whose frequency is damped when filled with samples. This gives an indirect measure of mass, and since the volume of the tube is constant, the density is readily determined. The instrument is easy to operate and provides density measurements to four significant figures. A single determination takes about 10 minutes. Other density measurement techniques would require much greater time and skill to achieve comparable accuracy.

Determination of Bitumen, Naphtha, Water and Solids Content of Centrifuge Feed and Product Samples

Scope: This method determines the bitumen, naphtha, water and solids content of feed and product samples originating from dilution centrifuging operations.

Summary: The sample is separated into hydrocarbon, water and solids by refluxing with toluene in a solids extraction apparatus. Condensed solvent and co-distilled water are continuously separated in a trap, the water being retained in the graduated section. The solvent recycles through the extraction thimble to dissolve the hydrocarbon. The resulting naphtha/bitumen/solvent and non-filtered solids are separated by centrifuging. The solids are determined gravimetrically by combining the contributions for solids retained by the extraction thimble and for non-filtered solids. The bitumen is determined spectrophotometrically at 600 nm by comparison with a bitumen standard. Naphtha is calculated by difference.

Background: This method is identical to Method 2.9 except that it distinguishes the amounts of bitumen and naphtha in the hydrocarbon phase by spectrophotometry.

An alternative method to distinguish bitumen and naphtha in the sample is the gas chromatographic procedure described in Method 3.3. That method determines the naphtha in the hydrocarbon phase and the bitumen is calculated by difference. However the technique requires an additional sample of the process stream.

Interferences:

1. The accuracy of the spectrophotometric method is determined by the similarity of the bitumen in the sample to the reference bitumen. This similarity is ensured by using reference bitumen from the specific process stream that is to be analyzed.
2. Naphtha, if too highly colored, will contribute to the bitumen absorbance causing erroneous high bitumen values and correspondingly low naphtha values.

Safety Considerations:

1. Isopropyl alcohol — irritant to the skin and respiratory tract. Highly flammable.
2. Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.

Apparatus, Reagents, Materials:

1. Condenser — a straight tube condenser having a water jacket at least 400 mm long. West type condenser with 24/40 standard taper male joint as specified by ASTM E 123 is suitable.
2. Water trap — the trap having 24/40 standard taper joints shall be of 10 mL or 25 mL capacities. The designs are taken from ASTM E 123. The 10 mL trap has 0.1 mL scale divisions and a maximum scale error of 0.05 mL. The 25 mL trap has 0.1 mL scale divisions and a maximum scale error of 0.05 mL from 0 to 1 mL. From 1 to 25 mL, scale divisions are 0.2 mL with a maximum scale error of 0.1 mL.
3. Kettle — a heat-resistant glass vessel having a nominal capacity of 500 mL. The neck shall be a minimum of 250 mm long, including a 55/50 standard taper female joint to accommodate a kettle-to-trap adapter.
4. Kettle-to-trap adapter — the lower part of the adapter has a 55/50 standard taper male joint with a perforated downcomer extending below the ground glass surface. The upper part of the adapter is fitted with a 24/40 standard taper female joint.
5. Extraction thimble — Whatman 43 x 123 mm cellulose thimble, single thickness.
6. Thimble basket — a corrosion-resistant basket to support the thimble. See Figure 1. Fabrication from 1.5 mm diameter nichrome or chromel wire using a silver solder bottom joint is suitable.

7. Solvent distributor — a corrosion-resistant screen to snugly fit over the open end of the thimble.
8. Heating mantle — 250 W, to accommodate 500 mL kettle.

The assembled extraction apparatus is shown schematically in Figure 2.

9. Kimwipes — Type 900-S.
10. Weighing bottles — short form, 50 x 140 mm of borosilicate glass, with a 55/12 ground glass rim.
11. Centrifuge — 87 rev/s max, 4275 x G, 6 x 1000 mL capacity, complying with Class 1 Group D explosion-proof requirements, equipped with an eight place horizontal head, trunion rings and shields.
12. Centrifuge tubes — 100 mL, conical, graduated as described in ASTM D 96.
13. Volumetric flasks — 1000 mL, Class A.
14. Double beam spectrophotometer set at 600 nm.
15. Two matched, fused silica spectrophotometric cells of 10 mm path length.
16. Syringe — 5 mL, glass, Luer-Lok tip.
17. Disposable filter assemblies — Millipore Millex filters, 0.45 μm, 25 mm diameter, catalogue No. SLHA 025 OS.
18. Evaporating dishes — 250 mL, porcelain.
19. Top loading balance to ±0.001 g, 320 g capacity.
20. Drying oven — forced draft, set at 120°C.
21. Desiccator.
22. Reagents:
    Isopropyl alcohol, A.C.S. reagent grade.
    Toluene, A.C.S. reagent grade.

Procedure: Sample Handling

1. Sample sizes should range from 40 to 50 g.
2. Prior to use, insert 3 rolled Kimwipes into each of a quantity of new thimbles. Place each thimble in a weighing bottle and dry, uncapped, for 1 hour at 120°C. Cap the weighing bottles and store in a desiccator until needed.
3. Weigh the weighing bottles plus thimbles to the nearest 0.001 g. Remove the Kimwipes and place the thimble in its support basket. Mount the thimble and basket in the neck of the kettle by spreading the basket's attaching wires. Clean the outside of the sample container and weigh to the nearest 0.01 g. Transfer the sample to the thimble, wash with toluene until clean, and wipe dry with the Kimwipes. Place the Kimwipes in the thimble. Weigh the empty bottle.
4. Fill the kettle with toluene to a volume of approximately 200 mL. Cover the thimble with the solvent distributor and attach the basket to the adapter. Select a 10 or 25 mL trap, depending on the anticipated water content of the sample, and assemble the apparatus as shown in Figure 2, ensuring that all connections are vapor tight.

Extraction

5. Apply heat and adjust to maintain the reflux rate such that liquid does not overflow the thimble. Continue refluxing for 30 minutes after no water is visible in any part of the apparatus except the trap, and the solvent dropping from the thimble is colorless. Discontinue heating and when refluxing has stopped, add three drops of isopropyl alcohol around the inside rim of the condenser to bring water droplets adhering to the glass surface of the condenser down into the trap.

Water

6. Allow the trap and contents to cool to room temperature. Estimate the volume of water to 0.01 mL for 10 mL traps, or to 0.05 mL for 25 mL traps.

Solids

7. Disassemble the apparatus, remove the thimble from its support and return it to its original weighing bottle. Dry the thimble, uncapped, for 3 hours at 120°C. Cool the capped assembly in a desiccator and weigh to the nearest 0.001 g.

Non-filtered Solids

8. Transfer the naphtha/bitumen extract and non-filtered solids mixture remaining in the kettle to a 1000 mL volumetric flask. Thoroughly rinse the kettle with toluene, adding the washings to the flask. Invert the flask several times to suspend the fines and immediately transfer 75 mL to a clean centrifuge tube preweighed to the nearest 0.0001 g. Stopper the tube and centrifuge at 33 rev/s for 20 minutes. Carefully decant the naphtha/bitumen/solvent solution. Rinse the inner walls of the tube with toluene, being careful not to dislodge any particles. Discard the washings. When clean, dry the centrifuge tube at 120°C for 1 hour. Cool in a desiccator and weigh.

Preparation of Standard Bitumen

9. Extract with toluene approximately 30 g of froth using a solids extraction apparatus as described in Figure 2. Centrifuge the total extract at 33 rev/s for 20 minutes. Decant the bitumen/toluene solution into a suitable evaporating dish and evaporate the solution until the residual toluene is between 1 and 5%. The bitumen at this point flows very slowly when the dish is tilted. Remove approximately 1 g and determine the residual toluene as described in Method 2.7.

Bitumen Determination

10. Dissolve approximately 1.3 g of standard bitumen weighed to the nearest 0.001 g, in toluene and dilute to 1000 mL in a volumetric flask. Correct the bitumen weight for the residual toluene.

11. Fill a 10 mm cell with a portion of this solution using a syringe equipped with a 0.45 μm filter assembly. Record the absorbance at 600 nm versus toluene.

12. Dilute a portion of the naphtha and bitumen solution 1:40 with toluene. Fill a 10 mm cell with a portion of this solution using a syringe equipped with a 0.45 μm filter assembly. Measure the absorbance at 600 nm versus toluene.

Calculations: The bitumen, naphtha, water and solids content of the sample and naphtha to bitumen ratio are given by:

$$\% \text{ Water} = \frac{V}{W} \times 100$$

$$\% \text{ Solids} = \frac{(S + 13.33A)}{W} \times 100$$

$$\% \text{ Bitumen} = \frac{(\text{Absorbance of Sample})\ (F)\ (40)}{W} \times 100$$

$$\% \text{ Naphtha} = 100 - (\text{wt\% Water} + \text{wt\% Solids} + \text{wt\% Bitumen})$$

$$\text{Naphtha/Bitumen Ratio} = \frac{\text{wt\% Naphtha}}{\text{wt\% Bitumen}}$$

where: V = volume of water in trap, mL. The density of water is assumed to be 1.0 kg/L.
W = weight of sample, g
S = weight of solids recovered in thimble, g
A = weight of fines in centrifuge tube, g

$$F = \frac{\text{Grams Standard Bitumen/Liter}}{\text{Absorbance at 600 nm}}$$

Precision: Estimates depicting the reliability of replicate determinations for total hydrocarbon, water, solids, and naphtha to bitumen ratio on a centrifuge feed sample are tabulated below:

	Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
Hydrocarbon	78.62	±0.74	0.94%
Water	18.55	±0.72	3.90%
Solids	2.83	±0.04	1.39%
Naphtha/Bitumen Ratio	0.70	±0.01	1.87%

The above data was derived from a set of 5 subsamples obtained as described in Method 1.6. Contributory variance due to subsampling is incorporated in these estimates.

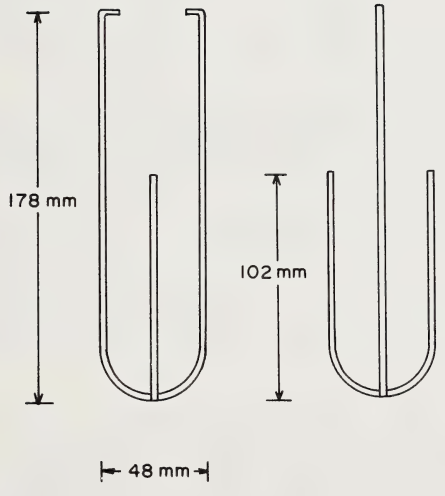


FIGURE 1: EXTRACTION THIMBLE BASKET

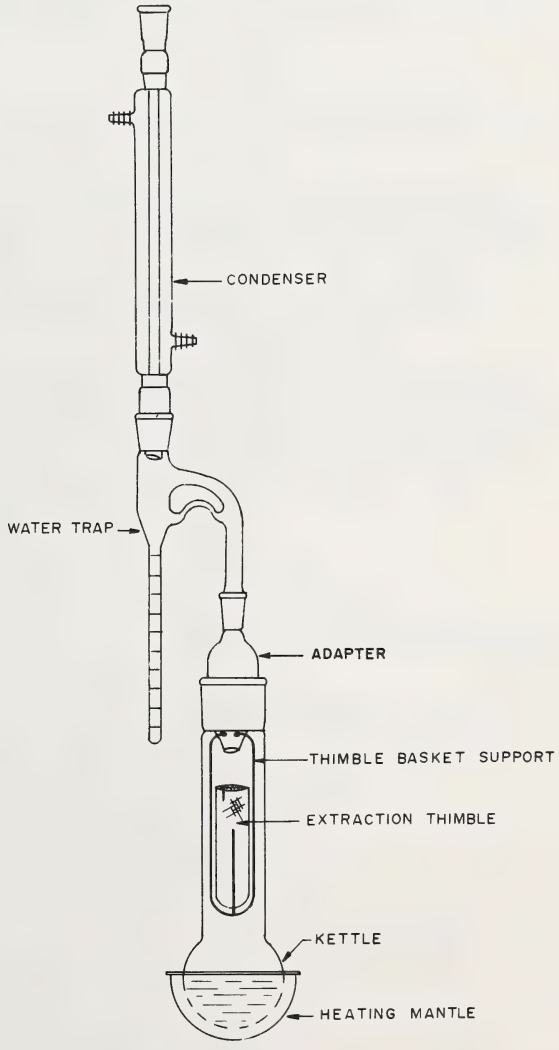


FIGURE 2: EXTRACTION APPARATUS

Determination of Bitumen, Naphtha, Water and Solids Content of Centrifuge Tailings Samples

Scope: This method determines the bitumen, naphtha, water and solids content of froth treatment tailings samples. Preferred sample sizes range from 250 to 600 g, although the method may be modified for smaller samples.

Summary: The acidified sample is separated into hydrocarbon, water and solids by refluxing with benzene in a solids extraction apparatus. Condensed solvent and co-distilled water are continuously separated in a trap. The water is drained from the lower portion of the trap while the solvent recycles through the extraction thimble to dissolve naphtha and bitumen. When the extraction is complete, the clean solids retained in the thimble are dried and weighed. The hydrocarbon extract is analyzed spectrophotometrically for naphtha and bitumen. The absorbance of the extract is measured in the infrared at 2924 cm^{-1} and in the visible at 600 nm. By measuring the absorbances of standard naphtha and bitumen at the two wavelengths, the naphtha and bitumen contents of the sample are calculated. Water is determined by difference.

Background: This method is similar to Method 2.11 but employs benzene as the extraction solvent in order to accommodate the spectrophotometric analysis of naphtha and bitumen. The determination of both naphtha and bitumen is accomplished by measuring the absorptivity of each absorbing species at the two designated wavelengths, and solving simultaneous equations. Toluene cannot be used in this determination since it interferes with the absorbance of 2924 cm^{-1}. No chemical separation of the naphtha/bitumen/benzene solution is needed since specificity is provided by the spectrophotometric measurements. The addition of acid provides sufficient flocculation of the solids that a non-filtered solids correction is not required. However the extract is filtered prior to the spectrophotometric measurement.

An alternative method of analysis, based on duplicate samples, may also be applied to centrifuge tailings. With one sample, the naphtha content of tailings is determined by Method 3.3. The other sample is extracted with toluene on a solids extraction apparatus to determine the solids, remove water from the sample, and provide a naphtha/bitumen/toluene extract. The extract is then distilled in the solids extraction apparatus with naphtha and toluene being removed from the trap. Fresh toluene is added to maintain sufficient solvent in the kettle. This distillation is continued until the naphtha is removed from the bitumen. The bitumen content of the sample is then determined gravimetrically by evaporating an aliquot of the bitumen/toluene solution. The removal of naphtha from the bitumen may be confirmed by Method 3.3. In practice, however, Method 3.3 is used to establish the length of the distillation required to remove the diluent naphtha in use.

The benzene and trichloroethylene used in the present method are suspected carcinogens. Zero exposure to these solvents is therefore recommended. The method is included in this collection as a classical method which illustrates the spectrophotometric finish for determining naphtha and bitumen. The alternative method, described above replaces benzene with toluene. From a safety viewpoint, the alternative procedure is preferred. The classical spectrophotometric method is presented here since the naphtha determination by gas chromatography is described in Method 3.3. Also, modifiction of this method to replace benzene by toluene and to determine bitumen gravimetrically (Method 2.7) is straightforward.

Interferences: Non-homogenity of bitumen limits the accuracy of the spectrophotometric determination of naphtha and bitumen. It has been shown that the absorbance of bitumen at 600 nm is due in large part to the presence of asphaltenes. Since the asphaltene content of bitumen may vary depending on oil sand type and process stream, the absorbance of bitumen solutions of equal concentration will also vary. A second source of variation arises from the fact that asphaltene solutions of equal concentration also display variable absorbance. Thus the selection of froth as the standard bitumen reference material for this method is a serious limitation.

Safety Considerations:

1. Benzene — highly toxic and a suspected carcinogen. Employ strict precautions to prevent inhalation and skin absorption. Extremely flammable.
2. Hydrochloric acid — highly toxic by inhalation. A strong irritant to eyes and skin.
3. Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.
4. Trichloroethylene — a suspected carcinogen. Employ strict precautions to prevent inhalation and skin absorption.

Apparatus, Reagents, Materials:

1. Condenser — an indented tube condenser having a water jacket at least 535 mm long with a 29/42 standard taper male joint at the base.
2. Water trap — constructed to continuously separate water and solvent. The trap portion, which is approximately 25 mm in diameter and 220 mm long, has a volume of about 130 mL. The lower end is fitted with a stopcock for removal of water while the upper section has a 29/42 standard taper female joint to accommodate the condenser. The downcomer has a 103/60 standard taper male joint for connection to the kettle and is perforated with 3 mm diameter holes below the ground glass.
3. Kettle — a heat-resistant glass vessel having a capacity of 2000 mL. The neck has a minimum length of 390 mm and includes a 103/60 standard taper female joint.
4. Extraction thimble — Whatman 85 x 200 mm cellulose thimble, single thickness.
5. Thimble basket — a corrosion-resistant basket to support the thimble. See Figure 1. Fabrication from 3 mm diameter nichrome wire using a silver solder bottom joint is suitable.
6. Solvent distributor — corrosion-resistant, as shown in Figure 2.
7. Heating mantle — 500 W, to accommodate 2000 mL kettle.

The assembled extraction apparatus is shown schematically in Figure 3. If samples are less than 100 g then the extraction apparatus described in Method 2.7 is used with the exception that the lower end of the water trap is fitted with a drain cock. Volumes employed in the following procedure are then gauged accordingly.

8. Kimwipes — Type 1300.
9. Supply of 800 mL beakers.
10. Volumetric flasks — 10, 100, and 1000 mL, Class A.
11. Centrifuge — 87 rev/s max, 4275 x G, 6 x 1000 mL capacity, complying with Class 1 Group D explosion-proof requirements, equipped with an eight place horizontal head, trunion rings and shields.
12. Centrifuge tubes — 100 mL, conical, graduated as described in ASTM D 96.
13. Double beam infrared spectrophotometer.
14. Sodium chloride cells — 0.25 mm path length, matched.
15. Double beam spectrophotometer set at 600 nm.
16. Fused silica cells — 10 mm path length, matched.
17. Syringe — 5 mL, glass, Luer-Lok tip.
18. Disposable filter assemblies — Millipore Millex filters, 0.45 μm, 25 mm diameter, catalogue no. SLHA 025 OS.
19. Balances:
    Top loading to ±0.01 g, 1200 g capacity.
    Analytical balance.
20. Drying oven — forced draft, set at 120°C.
21. Desiccator.

22. Reagents:
    Benzene, A.C.S. reagent grade.
    Hydrochloric acid, A.C.S. reagent grade.
    Toluene, A.C.S. reagent grade.
    Trichloroethylene, A.C.S. reagent grade.
23. Distilled water.

Procedure: Sample Handling

1. Insert three Kimwipes into thimble, place the thimble into an 800 mL beaker and weigh to the nearest 0.01 g.
2. Clean the outer walls of the sample container and lid. Weigh to the nearest 0.1 g. Add 2 or 3 drops of concentrated hydrochloric acid to the sample and mix with a spatula. Then add approximately 100 mL of benzene to the sample and stir until all oil adhering to the walls of the container is dissolved.
3. Remove the Kimwipes from the thimble, insert the thimble into a thimble basket and mount the basket by its support into the neck of a kettle. Add approximately 700 mL of benzene to the kettle by pouring it through the thimble.
4. Restir the sample and while it is still in motion transfer to the thimble. Wash the container with benzene to remove all the oil. Add the washings to the thimble. Transfer the bulk of the remaining solids by scraping with a spatula. Finally, rinse and transfer remaining solids with distilled water. Clean and dry the container and lid with the Kimwipes and place them in the thimble. Weigh the container and lid.

Extraction

5. Assemble the extraction apparatus as shown in Figure 3, ensure all joints are vapour tight, and begin refluxing. Drain and discard water from the trap when it nears the trap overflow. Do not remove any solvent. The extraction is complete when the level of water in the trap is stationary and solvent dripping from the thimble is clear. Terminate the extraction and allow the apparatus to cool.

Solids Determination

6. Disassemble the extraction apparatus, pour the solvent retained in the water trap into the kettle, transfer the thimble to its 800 mL beaker, and dry for a minimum of 4 hours at 120°C. Cool and weigh. Pour the naphtha/bitumen/solvent extract into a 1000 mL volumetric flask and dilute to volume with benzene.

Bitumen Calibration

7. Prepare standard bitumen by extracting 30 g of froth with benzene on a solids extraction apparatus. Centrifuge the extract at 33 rev/s for 20 minutes and evaporate benzene from the resulting solution.
8. Prepare a 100 mL stock solution of 10 g toluene-extracted froth bitumen containing less than 0.5% toluene (a) in trichloroethylene. Also prepare a 5 mL stock solution of 0.50 g benzene in trichloroethylene.

   Prepare standards by combining the required volume of benzene solution with sufficient bitumen solution to make 10 mL as outlined in the following table.

Benzene Concentration (wt%)	Volume of Benzene Stock Solution (mL)
0.5	0.05
1.0	0.10
2.0	0.20
3.0	0.30
4.0	0.40
5.0	0.50
7.0	0.70
10.0	1.00

Ready the infrared spectrophotometer. Fill the reference cell with trichloroethylene and place in the reference beam. Fill the sample cell with each calibration standard and record the scans from 715 to 645 cm^{-1}. Flush the sample cell with trichloroethylene and air dry between each sample. Determine the net absorbance of each standard by drawing a baseline tangent on either side of the absorption peak at 680 cm^{-1} and subtracting the baseline absorbance from the gross absorbance.

Prepare a calibration curve by plotting the net absorbance of each standard versus its wt % benzene on rectangular coordinate paper. Draw the best fit through the points.

9. Take 1 g of the bitumen prepared in step 7 and dilute to 10 mL with trichloroethylene. Determine the net absorbance at 680 cm^{-1} and record the wt % benzene from the calibration curve prepared in step 8.

10. Using benzene as solvent prepare a 2.0 g/L solution of the standard bitumen prepared in step 7. Allow for the residual benzene determined in step 9 when preparing this solution.

    Using a syringe equipped with a 0.45 μm filter assembly, transfer some of the standard bitumen solution to a 0.25 mm path length infrared cell. Record the infrared spectrum from 3500 to 2400 cm^{-1} versus benzene in the reference beam. Measure the net absorbance of the solution at 2924 cm^{-1}.

    Determine the absorbance of the filtered standard bitumen solution versus a benzene reference at 600 nm.

Naphtha Calibration

11. Prepare a standard solution by diluting 2.0 g of naphtha to one liter using the same naphtha as contained in the samples. Measure the net absorbance of this solution at 2924 cm^{-1} and at 600 nm with benzene as the reference.

Naphtha and Bitumen Determination

12. Determine the net absorbance of the sample extract from step 6 at 2924 cm^{-1} and 600 nm using the same cells as for the standards and using benzene as the reference. If the absorbance of the extract is greater than 0.50 for either wavelength, dilute with benzene as required and back calculate to the absorbance without dilution.

Calculations: The bitumen,naphtha, water and solids content of the sample and naphtha to bitumen ratio are given by:

$$\% \text{ Bitumen} = \frac{[\ (A_1)(AN_2) - (A_2)(AN_1)\ ]\ (b)}{[\ (AN_2)(AB_1) - (AN_1)(AB_2)\ ]\ (W)} \times 100$$

$$\% \text{ Naphtha} = \frac{[\ (A_1)(AB_2) - (A_2)(AB_1)\ ]\ (n)}{[\ (AB_2)(AN_1) - (AB_1)(AN_2)\ ]\ (W)} \times 100$$

$$\% \text{ Solids} = \frac{S}{W} \times 100$$

$$\% \text{ Water} = 100 - (\text{wt \% Solids} + \text{wt \% Naphtha} + \text{wt \% Bitumen})$$

$$\text{Naphtha/Bitumen Ratio} = \frac{\text{wt \% Naphtha}}{\text{wt \% Bitumen}}$$

where:
- W = weight of sample, g
- S = weight of solids recovered in the thimble, g
- A_1 = absorbance of extract at 2924 cm^{-1}
- AB_1 = absorbance of standard bitumen solution at 2924 cm^{-1}
- AN_1 = absorbance of standard naphtha solution at 2924 cm^{-1}
- A_2 = absorbance of extract at 600 nm
- AB_2 = absorbance of standard bitumen solution at 600 nm
- AN_2 = absorbance of standard naphtha solution at 600 nm
- b = weight of bitumen (approx. 2.0 g) used to make the standard bitumen solution, g
- n = weight of naphtha (approx. 2.0 g) used to make the standard naphtha solution, g

If the absorbance of the standard naphtha solution at 600 nm is zero then the above equations reduce to:

$$\% \text{ Bitumen} = \frac{(A_2)(b)}{(AB_2)(W)} \times 100$$

$$\% \text{ Naphtha} = \frac{[\,(A_1)(AB_2) - (A_2)(AB_1)\,]\,(n)}{(AB_2)(AN_1)(W)} \times 100$$

Precision: The precision of the analysis is primarily governed by the repeatability of the spectrophotometric measurement for bitumen and naphtha content. Typical precision values obtained for a set of 6 centrifuge tailings subsamples prepared as described in Method 1.6 are reported below:

	Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
Hydrocarbon	1.26	±0.06	5.11%
Water	94.05	±0.19	0.20%
Solids	4.69	±0.20	4.37%
Naphtha/Bitumen Ratio	1.03	±0.25	24.27%

Estimates incorporate variability due to subsampling.

Comments: a. The determination of residual toluene is described in Method 2.7

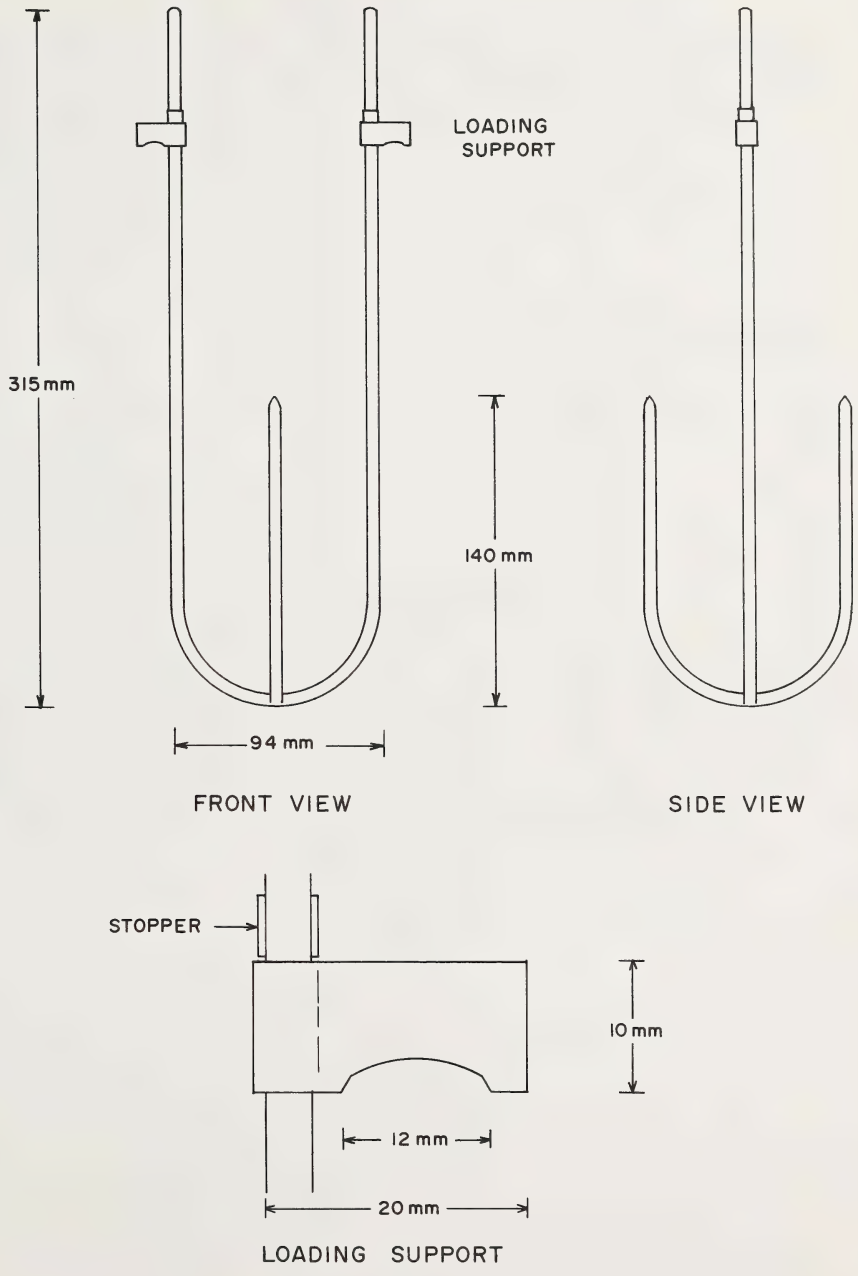


FIGURE 1: EXTRACTION THIMBLE BASKET

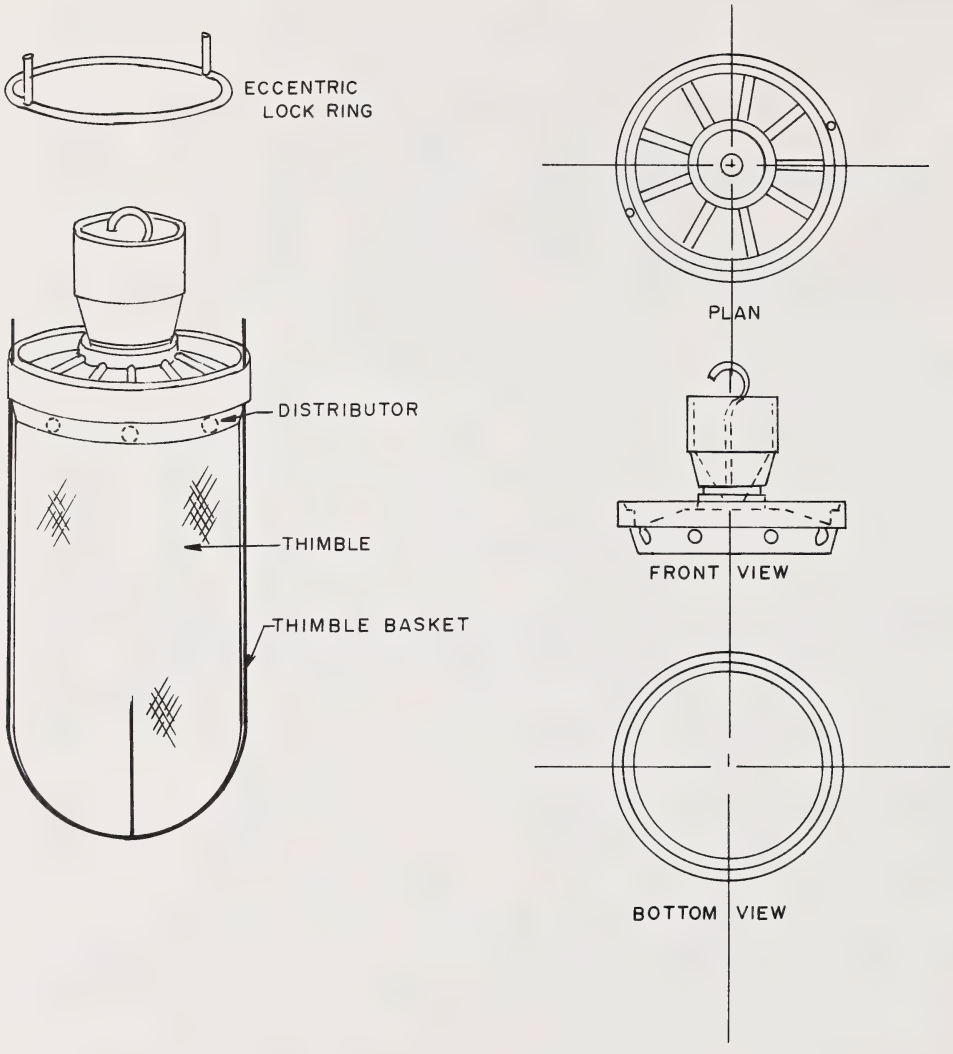


FIGURE 2: THIMBLE ASSEMBLY AND SOLVENT DISTRIBUTOR

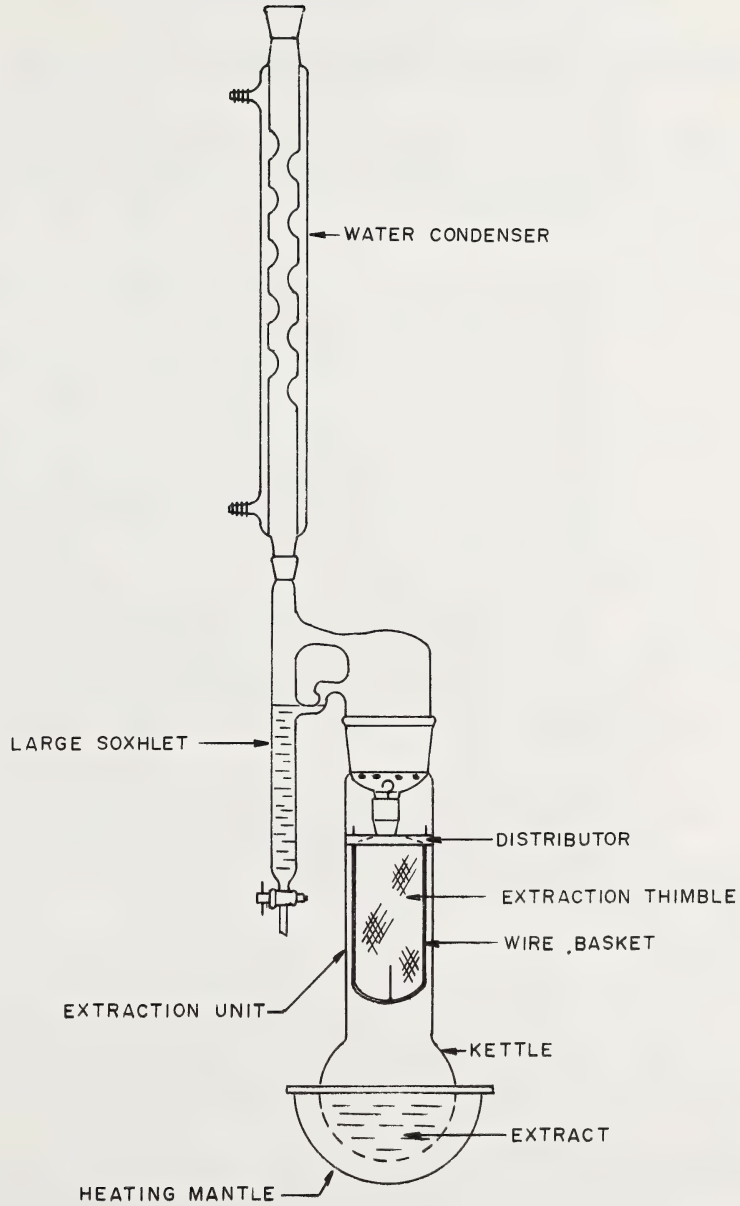


FIGURE 3: EXTRACTION APPARATUS

Quantitative Analysis of Naphtha in Froth Treatment Streams by Gas Chromatography

Scope: This method determines the naphtha content of samples from dilution centrifuging operations. The samples covered include feed product and tailings.

Summary: Samples are prepared to give a solution of naphtha and bitumen in 1,2,3,4-tetrahydronaphthalene which contains a known amount of anisole as internal standard. An aliquot is injected into a gas chromatograph which separates the sample components and provides a quantitative measure of the naphtha content of the sample.

Background: A separation is required to accurately measure the naphtha content of diluted bitumen samples. While procedures such as ASTM D 86, D 332, D 2887 and D 3528 may be suitable, the lengthy analysis time renders such approaches impractical for routine applications. By using a two column gas chromatographic system, an accurate analysis can be achieved in a reasonable time. The gas chromatography system employs two columns of complementary polarity to separate the sample components. The first column has low polarity for saturate and aromatic hydrocarbons. It permits material in the boiling range of naphtha to pass to the second column. The solvent and any volatile components from the bitumen are removed from the system by backflushing to an external vent. The second column is extremely polar and separates the internal standard from the naphtha to generate precise analytical data.

The pneumatic configuration employed in the system (Figure 1) was chosen to minimize any baseline disturbance associated with cycling the system from the series to the backflush mode of operation. This is achieved by maintaining a constant pressure at the head of the second column to maintain constant carrier gas flow to the detector. The stable baseline permits high sensitivity operation with low volume injections. The small samples minimize fouling of the system with non-volatile bitumen residue.

Due to the viscous nature of diluted bitumen samples and the non-homogeneous character of tailings samples, a solvent is used to prepare the samples for gas chromatographic analysis. Potential interference from the solvent is eliminated by using a high boiling aromatic compound as solvent. The solvent is removed from the system in the backflush and is not detected.

Interferences:

1. Bitumen contains a small amount of material which is indistinguishable from naphtha. In this analysis it is considered as naphtha. This is compatible with commercial naphtha recovery operations.
2. The gas chromatographic system is calibrated with a typical naphtha. Minor changes in the naphtha will not seriously affect the calibration. Drastic changes in the nature of the naphtha would affect the results, but the unusual appearance of the chromatogram will alert the operator in such cases.

Safety Considerations:

1. Hydrogen gas — extremely flammable, high explosion hazard.
2. 1,2,3,4- Tetrahydronaphthalene — moderately toxic by inhalation and skin absorption. Highly flammable. May form peroxides during storage.
3. Anisole — highly toxic by inhalation and skin absorption. Highly flammable. May form peroxides during storage.

Apparatus, Reagents Materials:

1. Gas Chromatograph, Hewlett-Packard 5830 with the following options:
   i) flame ionization detector;
   ii) heated flash vaporization injection ports with disposable glass liners;
   iii) four port flow switching valve (Valco CV-4-HPa) in heated valve oven with automatic actuator;

iv) auxillary pressure regulator 0-690 kPa.

Hewlett-Packard Co., 1501 Page Mill Road, Palo Alto, CA 94304.

2. Columns — all 2 mm ID stainless steel. Column #1 - 0.6 m long, 10% Siponate DS-10 on Chromosorb W AW (80/100 mesh). Column #2 - 1.8 m long, 20% OV-275 on Chromosorb P AW (100-120 mesh).
3. Analytical balance.
4. Centrifuge — 87 rev/s max., 4275 x G, 6 x 1000 mL capacity, complying with Class 1 Group D explosion-proof requirements.
5. High speed centrifuge — 333 rev/s max., 39000 x G, 8 x 52 mL capacity, 8 place angle head.
6. Steel centrifuge tubes — 50 mL, with caps.
7. Reciprocating shaker — 40 mm stroke, set at 3 cycles/s.
8. 1,2,3,4- Tetrahyronaphthalene — 99%.
9. Anisole — 99%.
10. Helium — 99.995%, oxygen and moisture free.
11. Hydrogen — hydrocarbon free.
12. Air — hydrocarbon free.
13. Blend of equal volumes of normal paraffins from C_5 to C_{14}.
14. Syringe — 1.0 μL.
15. Disposable vials — Kimble 2 dram.
16. Disposable Pasteur pipets and bulbs.
17. Syringe cleaner — Hamilton 15370.

Preparation Steps: Preparation of Apparatus

Assemble the pneumatics of the gas chromatograph as shown in Figure 1. The following points are important to provide reliable service.

1. The flow switching valve must be maintained at column temperature or slightly warmer, and may be positioned in the column oven or in a separately heated valve oven.
2. The tubing that connects the injection port to the valve must be inside the column oven to prevent the solvent from condensing during the backflush.
3. The valve driver must be arranged so that the system is normally in a backflush mode between injections. The standard injection port contains dead space where solvent vapours can accumulate. These, if given sufficient time in a foreflush mode, can generate ghost peaks of unpredictable retention time.
4. The columns should be thoroughly conditioned before being installed. Overnight conditioning at 170°C is recommended. The columns should not be connected in series while being conditioned. They should be terminated with a short length (approx. 150 mm) of capillary tubing to prevent the back diffusion of air during conditioning. Helium flow of 0.50 mL/s should be maintained during this procedure.

Instrument Parameters

5. Set the following temperatures:
   - detector 250°C
   - injector 250°C
   - valve oven 170°C

Set the pressure regulator so no auxillary helium is delivered to the column junction from the regulator. Set the valve so both columns are in series.Set the oven temperature to 150°C, allow the system to equilibrate. Read the pressure at the column junction. Set the pressure regulator to deliver between 35 and 70 kPa above this pressure. Cycle the valve to establish a backflush through column #1. Measure the backflush flowrate and adjust the needle valve so that the backflush flowrate is approximately 1.0 mL/s.

6. Ignite the FID.
7. Set the valve to place columns in series and inject 0.01-0.02 μL of the C_5-C_{14} mixture. Record retention times and relative peak areas.
8. Set the time program to actuate backflush at 1.0 minute. Place columns in series and inject 0.01-0.02 μL of the C_5-C_{14} blend. The peaks due to C_{13} and C_{14} should be missing from the resulting chromatogram, while the C_{12} peak should be close to its original size. Adjust the time program if necessary to achieve this result.
9. Set the valve to place the columns in series and inject 0.02 μL naphtha (neat). Observe the resulting chromatogram at an attenuation of 2 (▲) 3. If peaks can be seen past three minutes, adjust the flow from the flow controller to deliver a somewhat lower flow and repeat the naphtha chromatogram. Record the times when the first and last naphtha peaks are observed. Time program the chromatograph to sum the area of all peaks due to the naphtha.
10. Inject a calibration standard and observe the chromatogram. There should be a clean separation between the naphtha and the internal standard. Adjust the slope sensitivity parameter of the integrator to accurately detect the anisole peak as observed at an attenuation of 2 (▲) 3. Record the time when the anisole is completely eluted. Allow this run to continue for 20 minutes to verify that no heavy peaks due to the 1,2,3,4- tetrahydronaphthalene solvent will occur. (See Figure 2 for typical chromatogram and operating parameters that have been successfully used).
11. Proceed with calibration and analysis of samples. (a,b,c)

Procedure:

1. Clean the 1.0 μL syringe by pumping 5-10 times into a small vial containing 1,2,3,4- tetrahydronaphthalene. Insert the syringe needle into the syringe cleaner and pump several times. Remove from cleaner and allow to cool.
2. Shake the sample. Slowly pump the syringe two or three times in the sample and withdraw 0.5 to 1 μL.
3. Wipe needle quickly with tissue.
4. Adjust volume to desired amount (0.1 or 0.5 μL). Wipe excess from needle tip with tissue. Withdraw plunger 0.3 to 0.5 μL to prevent sample from flashing onto outside of hot injection port.
5. Actuate valve to put columns into series.
6. At a reproducible time after actuating valve (3 to 5 seconds) inject sample and press START RUN button.

A. Heavy Hydrocarbon Samples

Calibration

7. Gravimetrically prepare a stock solution of approximately 5% (weight) anisole in tetrahydronaphthalene. Calculate the actual wt % anisole in this solution.
8. Prepare three calibration standards using known weights of a typical diluent naphtha and the stock 5% anisole/tetrahydronaphthalene solution. Prepare the standards using the following approximate volume proportions.

Standard	Volume Naphtha (mL)	Volume Blend (mL)
1	.75	4
2	1.00	4
3	1.25	4

Calculate the weight of anisole in each calibration standard. Calculate the ratio of weight naphtha/weight anisole for each standard.

9. Assay 0.1 μL of each of the three standards with the gas chromatograph. Record the areas corresponding to the naphtha and anisole. Calculate the ratio of area naphtha/area anisole.

10. Perform a linear regression calculation to correlate the area ratios to the weight ratios. The coefficient of determination, r^2, value must be at least $r^2 = 0.9999$. If necessary, prepare new standards and repeat. Record the slope and intercept.

Assay of Sample

11. Inspect the samples and determine if centrifuging is required to remove water and solids from the hydrocarbon phase. If necessary, centrifuge at 250 rev/s for 20 minutes in a closed tube.

12. Label and tare a two dram vial.

13. Transfer 0.5 to 1 mL of hydrocarbon phase into the vial using a disposable Pasteur pipet. Record the sample weight.

14. Add anisole/tetrahydronaphthalene solution of about twice the sample volume using a disposable Pasteur pipet. Weigh the amount of anisole/tetrahydronaphthalene added and calculate the weight of anisole added. Mix thoroughly by shaking.

15. Assay 0.1 μL of the sample with the gas chromatograph. Record the areas of the naphtha and the anisole.

B. Tailings Samples

Calibration

16. Gravimetrically prepare a stock solution of approximately 1% (weight) anisole in tetrahydronaphthalene. Calculate the actual wt % anisole in this solution.

17. Prepare three calibration standards using known weights of a typical diluent naphtha and the stock 1% anisole/tetrahydronaphthalene solution. Prepare the standards using the following approximate volume proportions.

Standard #	Volume Naphtha (μL)	Volume Blend (mL)
1	25	2
2	50	2
3	75	2

Calculate the weight of anisole in each calibration standard. Calculate the ratio of weight naphtha/weight anisole for each standard.

18. Assay 0.5 μL of each of the three standards with the gas chromatograph. Record the areas corresponding to the naphtha and anisole. Calculate the ratio of area naphtha/area anisole.

19. Perform a linear regression calculation to correlate the area ratios to the weight ratios. The coefficient of determination, r^2, value must be at least $r^2 = 0.9999$. If necessary, prepare new standards and repeat. Record the slope and intercept.

Assay of Sample

The samples are cold extracted with 1% anisole/tetrahydronaphthalene solution and naphtha is determined as wt % of the total sample.

20. Weight sample and jar.
21. Add approximately 20 mL of 1% anisole/tetrahydronaphthalene and weigh. Shake for 5 minutes on a mechanical shaker. Calculate the weight of anisole.
22. Centrifuge at 33 rev/s for 20 minutes. Collect 0.5 mL of extract in a vial.
23. Assay 0.5 μL of extract for naphtha content with the gas chromatograph. Record the areas of the naphtha and anisole.
24. Discard remainder of sample. Clean and weigh sample jar. Determine sample weight.

Calculations:

A. Heavy Hydrocarbon Samples

Calculate the weight % naphtha in the hydrocarbon phase as follows:

1. Determine the area ratio of the sample

$$\text{Area Ratio} = \frac{\text{Area Naphtha}}{\text{Area Anisole}}$$

2. Calculate the corresponding weight ratio using the slope and intercept values previously determined.

$$\text{Wt Ratio} = (\text{Area Ratio})(\text{Slope}) + (\text{Intercept})$$

3. Calculate the wt % naphtha in the sample

$$\text{Wt \% Naphtha} = \frac{\text{Wt Ratio} \times \text{Wt Anisole}}{\text{Wt Sample}} \times 100$$

B. Tailings Samples

Determine wt % naphtha by the calculation routine given for heavy hydrocarbon samples. Report naphtha content as wt % of the entire sample.

Precision: The variability associated with determining the naphtha content in replicate samples of diluted bitumen has not been evaluated. Data tabulated below, based on 6 injections of a naphtha in anisole calibration standard, indicates the typical precision attainable in the absence of subsampling error.

Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
36.13	±0.26	0.72%
1.03	±0.008	0.78%

Comments:

a. The most common problem with a system of this type is unacceptable precision. The most likely cause of such a problem is poor technique with the 1.0 μL syringe. It is important that the syringe be cleaned after every injection and given ample time to cool before attempting to inject the next sample. Sample volumes should be as closely repeated as is practical (a Chaney adaptor is useful). Vigorous pumping of the syringe should be avoided as this hastens failure of the internal seal in the syringe. Holding the needle with the fingers to guide it into the septum will cause the needle to expand and non-reproducible injections will result. A rhythm should be developed so that the sample is injected at a reproducible interval following the valve change that places the columns in series.

b. The septum should be changed frequently and the glass liner inspected and changed as required. Leaks in the septum can be easily recognized by the odor of tetrahydronaphthalene near the septum following an injection.

c. It is important to use a good quality of carrier gas that contains no air. Trace oxygen in the carrier will result in oxidation of the column packing and will be observable as a baseline "step" whenever the valve is changed. If necessary, suitable purification of the carrier should be done using an oxygen scrubber.

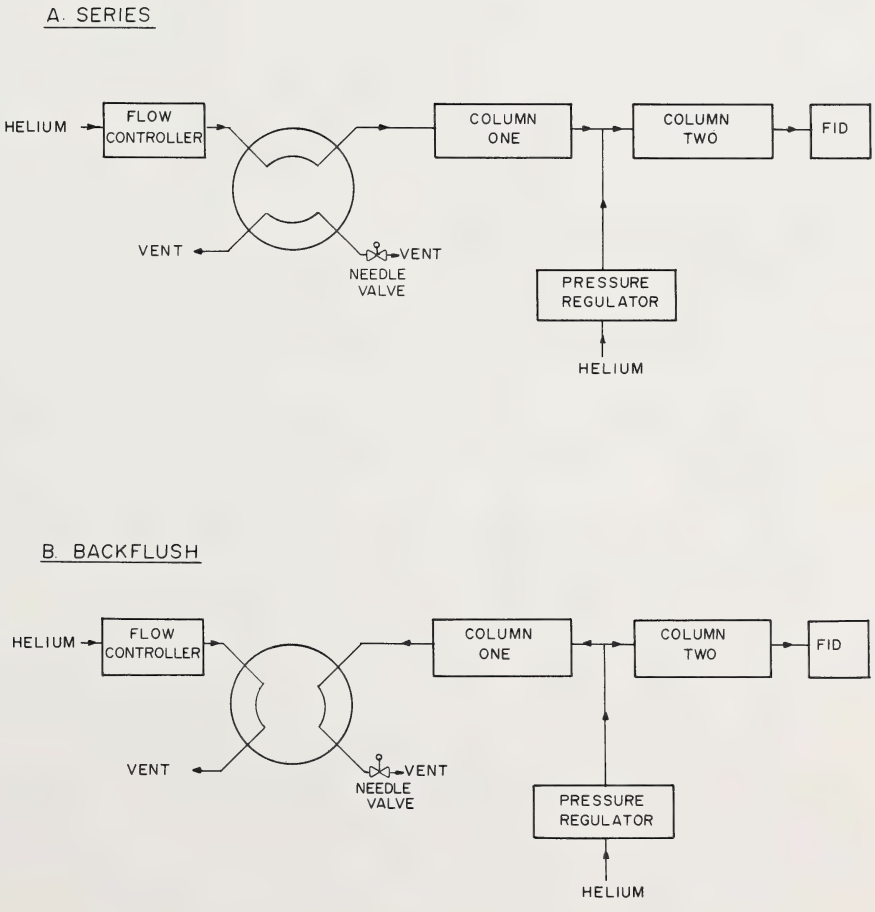
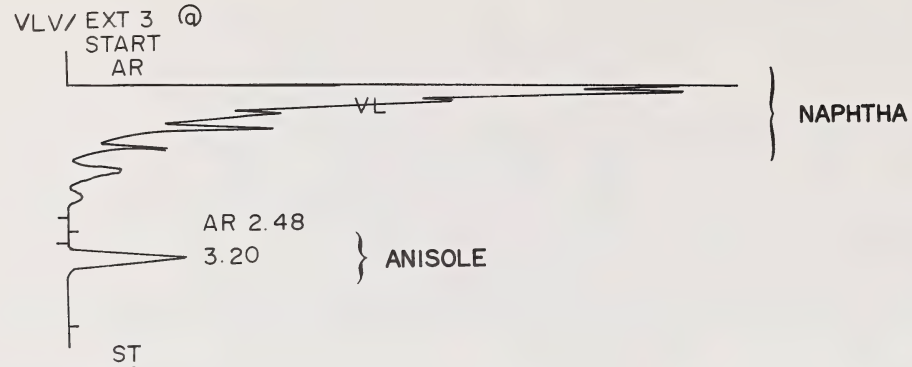


FIGURE 1 PNEUMATIC CONFIGURATION FOR NAPHTHA ANALYZER



hp 5830A
AREA %

RT	AREA	AREA %
2.48	7636000	92.671
3.20	603400	7.323

XF: 1.0000 E+0

TEMP I	150 150
TIME I	0.0
INJ TEMP	250 250
FID TEMP	250 250
TCD TEMP	0 107
AUX TEMP	170 170
OVEN MAX	400
CHT SPD	1.00
ATTN 2↑	12
FID SGNL	+B
SLP SENS	0.00
AREA REJ	1
FLOW A	29
FLOW B	30
OPTION	0

0.4	AREA REJ	0
0.9	VLV/ EXT-	3
2.5	AREA REJ	1
4.5	STOP	

FIGURE 2 TYPICAL CHROMATOGRAM AND OPERATING PARAMETERS

Determination of Water in Naphtha Samples by Karl Fischer Titration

Scope: This method determines water in the diluent naphtha used during froth treatment.

Summary: An aliquot of sample is coulometrically titrated with Karl Fischer reagent to a potentiometric end point.

Background: The water content of naphtha samples is primarily used as a process control measurement in froth treatment, augmenting API gravity and viscosity data for monitoring diluent feed quality. Typically the water content of diluent naphtha is within the range 0.1 - 2 wt %. Significant deviations may reflect operational upsets in the diluent recovery or preparation stages. Furthermore, water values must routinely be accounted for in evaluating mass balances and overall plant performance, although their contributory effects are generally minor.

The 74% toluene and 26% isopropyl alcohol solvent blend is chosen as solvent for the standards so that this procedure is similar to the water determination steps of Methods 2.8 and 2.10.

Interferences: Oxidizing and reducing agents, mercaptans, certain basic nitrogen compounds, or other materials that react with iodine interfere with the Karl Fischer titration (1,2). Although the extent of interference depends on the diluent naphtha quality, the interferences are considered trivial compared to the water content of the diluent naphtha used during froth treatment.

Safety Considerations:

1. Dimethyldichlorosilane — evolves toxic and corrosive fumes of hydrogen chloride upon contact with moisture. Avoid contact with skin, eyes, or clothing; do not breath fumes. Neutralize excess reagent by cautious addition of methanol.
2. Isopropyl alcohol — irritant to the skin and respiratory tract. Highly flammable.
3. Karl Fischer reagent — toxic by skin absorption and inhalation. Flammable.
4. Naphtha — flammable.
5. Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.

Apparatus, Reagents, Materials:

1. Photovolt Aquatest II Automatic Karl Fischer Titrator and accompanying vessel and generator solutions. Photovolt Corporation, 1115 Broadway, New York, NY 10010.
2. Push button adjustable syringe — 200 μL. Hamtilton CR700-200.
3. Six serum bottles — 125 mL, with Viton flange type stoppers and aluminum seals.
4. Six volumetric flasks — 100 mL, Class A.
5. Drying oven — forced draft, set at 110°C.
6. Desiccator.
7. Reagents:
   Acetone, A.C.S. reagent grade
   Dimethyldichlorosilane (DMDCS)
   Isopropyl alcohol, 99 mol %
   Methanol, A.C.S. reagent grade
   Toluene, A.C.S. reagent grade.
8. Molecular sieves — type 4A.
9. Analytical balance.
10. Distilled water.

Procedure: Solvent Blend Preparation

1. Fill a large closed container with 74% toluene and 26% isopropyl alcohol (volume %).
2. Add molecular sieves, type 4A, to the container and allow the solvent blend to dry for 24 hours. If the weather is unusually humid a longer drying time is required. Absolutely dry solvent (no reading on a Karl Fischer titrator) should be used to prepare the water standards so that their absolute water content will be known.
3. Determine the density of the blend (Method 3.6). A 74% toluene/26% isopropyl alcohol mixture has a density of 0.8440 kg/L at 20°C. If the density falls outside the range of 0.8435 to 0.8445 kg/L, adjust the solvent blend as follows:
   i) for densities greater than the permitted range, add isopropyl alcohol until the correct density is obtained.
   ii) for densities less than the permitted range, add toluene until the correct density is obtained.

Preparation of Water Standards

4. All glassware used is first treated with the silylating agent DMDCS to prevent adsorption of water on the glassware for the standard solutions.
   i) Clean volumetric flasks and serum bottles with a strong detergent. Rinse well with water and then with acetone. Dry in oven and desiccate until cool.
   ii) Immerse glassware in a 5-10% DMDCS solution (in toluene) for a few minutes. Rinse glassware with dry methanol, dry in oven and desiccate until cool. Keep glassware stoppered with stoppers or septa which have also been dried in a desiccator. Hydrogen chloride is liberated from DMDCS on contact with moisture. Therefore work in a fumehood and use gloves. Any DMDCS spills are easily neutralized with methanol.
5. Prepare six standard water solutions by weighing distilled water (to the nearest 0.0001 g) into 100 mL volumetric flasks. The solutions should contain approximately 0.25, 0.50, 0.80, 1.20, 1.60, and 2.00 g of water respectively. Use the dry 74% toluene/26% isopropyl alcohol blend as the solvent for these standard solutions. Mix the solutions well and transfer them to the prepared serum bottles. Immediately stopper and seal the bottles. These solutions should keep for several months.

Calibration of Karl Fischer Titrator

6. The Aquatest II Karl Fischer titrator and syringe should be calibrated daily. Adjust the syringe so that it delivers a volume of about 100 μL. Do no change this volume between running the standard and sample solutions on the titrator.
7. Rinse the syringe three times with the most dilute water standard. Allow a few minutes to ensure that the chamber of the syringe is at its equilibrium volume, fill the syringe and inject an aliquot into the titration cell of the instrument. Flip the switch to TITRATE and record the number displayed when the END light comes on. Zero the display on the titrator, refill the syringe with the same standard solution, inject this aliquot into the titration cell and record the reading from the titrator. Titrate a third aliquot of the standard solution in like manner. Then repeat this entire procedure for each successive standard solution. Determine the median titration value for each water standard. If the water readings for the 0.80 g of water standard vary by more than 15 μg, check instrument and syringe performance.

Analysis of Samples

8. Shake the sample. Rinse the Hamilton syringe three times with the sample. As in the calibration procedure, allow a few minutes before filling the syringe with the aliquot to be titrated. Fill the syringe, and inject this aliquot into the titrator. Flip the titrator switch to TITRATE. When the END light comes on record the value of the aliquot titer. Repeat the analysis a second time. If the two results do not agree well repeat a third time. (a)
9. Measure the density of the naphtha, e.g. by Method 3.6.

Calculations: The Karl Fischer titrator calibration data is subjected to a linear least squares regression to obtain the slope and the intercept for the graph of the median Karl Fischer titrator reading versus the water standard concentration in units of g H_2O/100 mL. Using this slope and intercept, any reading from the titrator can be converted to a water concentration by the following equations:

$$\text{Water Concentration (g/100 mL)} = \frac{\text{Karl Fischer Reading} - \text{Calibration Intercept}}{\text{Calibration Slope}}$$

or

$$\text{Water Concentration (wt \%)} = \frac{\text{Water Concentration (g/100 mL)}}{\text{Naphtha Density (kg/L)}}$$

Precision: Typical values depicting the repeatability of water in naphtha determinations performed in adherence to this procedure are:

Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
0.074	±0.012	16.22%
0.135	±0.020	14.81%
0.298	±0.016	5.37%
1.070	±0.057	5.33%

The above data are derived from six replicate subsample determinations at each weight % water level and hence incorporate errors due to sampling.

Comments:

a. The water reading for the sample should fall within the range covered by the calibration curve.

References:

1. ASTM. "Water in Liquid Petroleum Products by Karl Fischer Reagent." Annual Standards (1976), Part 24, Method D 1744.
2. Photovolt Corporation. Aquatest II Operating Manual. New York, NY, 1974.

Determination of the Viscosity of Froth Treatment Streams Using a Rotational Viscometer

Scope: This method determines the viscosity of the hydrocarbon portion of centrifuge feed, product, and diluent process samples. Measurements may range from 0.1 to 100 mPa·s and are conducted at 27°C.

Summary: The hydrocarbon portion of the sample is separated by centrifuging. A spindle is then immersed into the hydrocarbon liquid and rotated at constant speed. The torque required to maintain rotation is measured and converted to viscosity by means of a calibration factor characteristic of the spindle and the rate of rotation of the spindle.

Background: The torque required to rotate a spindle in a fluid at constant speed is directly proportional to the viscosity of the fluid (1). If the viscosity is independent of the speed of the spindle, the fluid is termed Newtonian. For non-Newtonian fluids the viscosity depends upon the speed of the spindle and is called apparent viscosity. Apparent viscosity measurements are only valid for the specific test conditions at which they were determined. Suspensions and emulsions are non-Newtonian fluids. In addition, their non-homogeneous nature makes viscosity measurements difficult. For diluent, feed, and product froth treatment process streams, these difficulties may be avoided by separating the emulsified water and suspended solids from the hydrocarbon phase by centrifuging.

An alternative method of measuring viscosity of hydrocarbons is the kinematic approach outlined in ASTM D 445. This method measures the time required for a fixed volume of liquid to flow under gravity through a capillary tube (2).

The viscosity of a fluid is a very sensitive function of temperature. As a rule of thumb, the viscosity of most materials will change by 10% for a change of 1°C. Thus for accurate and precise measurements good temperature control, e.g. ± 0.03°C of the test temperature, must be maintained.

Viscosity is an important parameter in the gravity separation of solids and water from hydrocarbon liquids. The lower the viscosity the more efficient the separation. Once the optimum diluent to bitumen ratio has been established for the separation process, it may be quickly and easily monitored by viscosity measurements.

Safety Considerations: Naphtha — flammable.

Apparatus, Reagents, Materials:

1. Brookfield Synchro-Lectric Viscometer — model LVF equipped with ultra-low adapter. Brookfield Engineering Laboratories Inc., 240 Cushing St., Stoughton, MA 02072. (a,b)
2. Constant temperature bath — capable of accommodating the spindle assembly and maintaining the desired test temperature within ± 0.03°C.
3. High speed centrifuge — 333 rev/s max., 39000 x G, 8 x 52 mL capacity, 8 place angle head.
4. Steel centrifuge tubes — 50 mL, with caps.
5. Syringe — 25 mL, graduated.
6. Supply of 50 mL vials.

Procedure:

1. Transfer 35-40 mL of sample to a centrifuge tube and spin at 250 rev/s for 20 minutes. Decant the hydrocarbon phase to a labelled vial and place in a constant temperature bath maintained at 27°C.
2. Attach the spindle to the eye-hook assembly of the viscometer. With a syringe transfer 22 mL of the centrifuged sample to the ultra-low adapter cup. Raise the cup to position the spindle in the sample and attach the cup to the adapter.
3. Immerse the spindle and cup in the constant temperature bath to the appropriate level. Allow the assembly to equilibrate. Ensure the viscometer is level.

4. Depress the clutch and turn on the viscometer motor. Select the appropriate spindle rotation rate for the anticipated viscosity of the sample using the table presented in the calculations and release the clutch. Allow the dial to rotate until the pointer stabilizes at a fixed position, e.g. 5 - 7 minutes. Depress the clutch and turn off the motor leaving the pointer in view. Record the viscometer reading.

Calculations: For the spindle rotation rate employed, deduct windage from the viscometer reading and multiply the corrected reading by the corresponding factor:

Viscosity Range (mPa·s)	Spindle Rotation Rate (rev/s)	Windage	Factor
0-10	1.0	0.4	0.1
0-20	0.5	0.1	0.2
0-50	0.2	—	0.5
0-100	0.1	—	1.0

Precision: Strict precision evaluations related to the repeatability of viscosity measurements on diluted bitumen samples have not been undertaken. Brookfield Engineering Laboratories quote a reproducibility of 0.02 mPa·s for readings within the range 0-10 mPa·s when using the UL Adapter.

Comments:

a. The viscometer may be employed for other sample types with viscosities exceeding 100 mPa·S by removing the ultra-low adapter and substituting appropriate spindles.

b. Proper operation of the viscometer may be confirmed through the use of viscosity standards marketed by the manufacturer of the rotational viscometer.

References:

1. Minard R.A. An Industrial Rotational Viscometer and its Use with Materials of Varying Complexity. Brookfield Engineering Laboratories Inc., 240 Cushing Street, Stoughton, MA.

2. ASTM. "Kinematic Viscosity of Transparent and Opaque Liquids," Annual Standards (1976), Part 23, Method D 445.

3. Brookfield Engineering Laboratories. The Brookfield U.L. Adapter. Data Sheet 034-b, Brookfield Engineering Laboratories Inc., 240 Cushing St., Stoughton, MA.

Determination of Hydrocarbon Density

Scope: This method determines the density of any homogeneous hydrocarbon material which may be handled with a syringe. Undiluted bitumen is excluded because its high viscosity precludes handling with a syringe.

Summary: This method utilizes an instrument which measures the total mass of a tube by determining its natural frequency of vibration. This frequency is a function of the dimensions and elastic properties of the tube, and the weight of the tube and contents. At constant temperature the only variable is the density of the tube's contents. Calibration with toluene and air provides the data for determination of the instrument constants which allow conversion of the natural frequency of vibration to sample density.

The sample is introduced into the densimeter tube with a syringe and, after allowing the sample and system to achieve thermal equilibrium, the density is read directly from the instrument display. Between samples the tube is cleaned and dried. The air density measurement is confirmed to ensure the tube is clean.

Background: The frequency of vibration of a freely oscillating U-shaped glass tube is described by the equation:

$$F = \frac{1}{2\pi}\sqrt{\frac{C}{M + \rho V}}$$

where: F is the frequency
C is the elastic constant of the tube
M is the mass of the hollow tube
ρ is the density of the tube contents
V is the internal volume of the tube

Calibration constants for the system may be defined by measurement of two materials for which the density is accurately known. After the calibration constants are entered into the instrument, the measured oscillation frequency is used by a built-in preprogrammed calculator to directly display density.

The Anton-Paar DMA 45 Densimeter used in this procedure is based on the above principles. In theory, it is accurate to $\pm 1.0 \times 10^{-4}$ kg/L for densities in the range 0.5 to 1.5 kg/L. In practice, the accuracy produced is dependent upon the accuracy of the standards, the ability to accurately control the temperature, and the ability of the operator to transfer a representative sample to the instrument.

Other methods require significantly greater time and skill to produce comparable accuracy.

Interferences:

1. All process samples contain solids and water at some level. These materials change the observed density. Water at 0.05 wt % or solids at 0.005 wt % will change the density by 0.001 kg/L.
2. Air bubbles in the sample will cause low and unstable readings.
3. Any foreign materials left in the syringe or U-tube will result in a contaminated sample. Checks are incorporated within the procedure for U-tube contamination.

Safety Considerations: Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.

Apparatus, Reagents, Materials:

1. DMA 45 Digital Densimeter — Anton-Parr K.G., A-8054 Graz, Postfach 17, Kamtner Strasse 322, Austria.
2. Syringe — 2 mL.
3. Luer Adapter, Anton-Parr #521003.
4. Circulating constant temperature bath, capable of ± 0.05°C stability.
5. Toluene — A.C.S. reagent grade.

Procedure:

Instrument Startup

1. The constant temperature bath must be set to the desired operating temperature and connected to the densimeter. If the bath temperature is less than 20°C above ambient temperature, a means of cooling the bath water must be provided.
2. The bath and densimeter should be on at least overnight to allow temperature stabilization.

Calibration

3. Set the display selector switch to "T".
4. Using a syringe, pump 5 to 10 mL of toluene through the measurement tube, introducing it at the lower port and allowing it to exit from the upper port.
5. Switch on the built-in air pump and connect the air pump to the upper port of the measuring tube. Allow air to flow through the tube until the display is stable.
6. Switch off the air pump. The readings should quickly (e.g. within 60 s) assume a constant value.
7. Repeat steps 4, 5, and 6 until the resulting readings are identical. Note the value as T_{air}.
8. Introduce toluene into the measurement tube. Turn the light on only long enough to check for bubbles. Record the reading when the display becomes stable. Note that the time needed depends upon how long it takes the sample to reach the system temperature. Blow the sample out with air.
9. Repeat step 8 until identical readings are obtained. Record the value as T_{tol}.
10. Compute the densimeter constants:

$$A = \frac{T^2_{tol} - T^2_{air}}{\rho_{tol} - \rho_{air}}$$

$$B = T^2_{air} - A\rho_{air}$$

where: ρ_{tol} and ρ_{air} are the densities of toluene and air at the system temperature (1).

11. Set the values for A and B into the calibration switches and set the display switch to "ρ".
12. Measure toluene and air to confirm the correct density readout.

Instrument Check

13. The DMA 45 should only require recalibration if the temperature is changed. Before starting to run samples each day, confirm correct measurement of air and toluene densities.

Sample Preparation and Measurement

14. If required, centrifuge the sample to remove solids and water from the hydrocarbon phase. Pipet the hydrocarbon from the water and solids.
15. Confirm a correct ρ_{air} reading. If this value is not obtained, clean and dry the measurement tube as in steps 19 and 20.
16. Draw 1.5 to 2 mL of sample into a syringe. Place the syringe in the lower tube port and introduce the sample. Check for bubbles by momentarily turning on the light and observing the tube carefully. Never leave the light on during a measurement.
17. Record the density when the display has stabilized.
18. Withdraw the sample back into the syringe. If necessary this sample can be retained for further analysis.
19. Rinse out the measurement tube with toluene. Dry to a constant reading using the air pump.
20. Turn off the air pump and take an air reading. If it is not identical to the standard reading repeat step 19.
21. Clean and dry the syringe.

Calculations: Not applicable.

Precision: Replicate determinations to evaluate the precision of density measurements on the hydrocarbon phases of process samples have not been conducted. For pure compounds, repeat measurements by the same operator typically agree within ±0.0001 kg/L. The variability observed among 9 operators measuring pure compounds is shown below.

	Mean Value (kg/L)	Standard Deviation (kg/L)	Relative Standard Deviation
Toluene	0.8670	±0.0004	0.04%
Isopropyl Alcohol	0.7859	±0.0002	0.02%
n-Heptane	0.6834	±0.0003	0.05%

Reference:

1. National Research Council. "International Critical Tables of Numerical Data, Physics, Chemistry and Technology." Volume 3, McGraw-Hill Book Co., 1928, p. 3, 29.

CHAPTER 4

PARTICLE SIZE ANALYSIS

Particle size distribution is highly important in oil sand processing and finds particular application at three stages of the process.

1. Experience has shown that the clay matter in oil sand seriously reduces bitumen recoveries in the hot water process. Means are available to neutralize the deleterious effect of clay but clearly a measure of the clay concentration must be available. Within the extraction system the particle size distribution dictates the fraction of the solids which are capable of settling out in the extraction vessel and thus being removed with the tailings. The remainder form a suspension in the extraction water phase, changing its effective density, viscosity, and the amount of solids carried with water into the froth. This has resulted in extensive particle size studies of oil sand and process streams.
2. Dilution centrifuging is used to separate most of the water and solids from the froth. This is done by first reducing the hydrocarbon viscosity by dilution, and then accelerating the settling process through the use of centrifuges. The centrifuges' ability to remove solids is directly related to the particle size distribution of the solids. Again, it is the settling properties of the solids which are of interest and particle size is used as the monitoring technique.
3. The solids removed by hot water extraction and dilution centrifuging are collected in a tailings pond. The coarse solids separate rapidly but the clays produce a stable sludge that settles only after several years. To ensure that sufficient clarified water is available for recycle to the process the tailings pond must be large. Rapid methods of sludge settling are currently being studied and tailings management in general is one of the most intense areas of oil sand research.

Clay is extremely fine ($< 2\mu m$) and is more difficult to measure than particles of larger size. Fortunately, it has been established that there is a good correlation between clay and particles smaller than 45 μm. This size is chosen as that of the smallest particles that can be measured by screens with acceptable precision and with reasonable ease. Besides screening, methods based on sedimentation and laser diffraction are also described.

Screening by Method 4.1 is basic in that it is a required step at either the 45 μm or 147 μm level for either of the other methods. Screens smaller than 45 μm have been used in the past, but they are impractical for routine work due to the long analysis time and extreme difficulty in producing repeatable, accurate data. Any but the most careful work can result in errors of 10 to 20%.

Sedimentation by Method 4.2 has the advantage of directly measuring the particles of normal interest and extends down to about 0.2 μm. On the other hand it is slower than laser diffraction. Of greater concern, however, is the fact that even very small amounts of oil in the measured sample result in serious cell problems which are very time consuming to resolve. Also, the sample suspension must be totally free of isopropyl alcohol even though that solvent is used extensively in the sample preparation.

The laser diffraction technique described in Method 4.3 is the most recent technology to become available. It is more tolerant of oil, not affected by isopropyl alcohol, and easier to operate than the sedimentation procedure. It will readily measure solids passing a 147 μm screen, but is blind to particles below one micron in size and overestimates plate-like particles such as clays.

The selection of a method must keep in mind the fact that neither Method 4.2 or 4.3 is clearly always best. Gradually the laser diffraction method is replacing sedimentation for routine use. The only area of concern is high-clay streams. However, even with these streams the laser diffraction method appears preferable for process applications.

Determination of ± 45 μm Particle Size Distribution by Screening

Scope: This method employs a wet screening technique to segregate solids into two size portions with ± 45 μm nominal diameter. The method may be extended to larger nominal diameters by the substitution of appropriate screens.

Summary: The hydrocarbon and water components of a sample are initially removed through consecutive washings with toluene and isopropyl alcohol. The resulting cleaned solids, dispersed in isopropyl alcohol, are passed through a 325 mesh sieve, i.e. 45 μm openings. Particles retained by the sieve and those emerging with the sieve effluent are dried, weighed, and expressed as a weight percent of the total solids content.

Background: Screen analysis is conceptually the simpliest of all particle size analysis, since particles are sorted according to whether or not they pass through a hole of known size. Two faults occur with this simple principle. First, the use of many holes to speed up the operation is limited by the ability to create openings of the same size. Secondly, in the analysis of many particles some small particles may not get an opportunity to drop through an opening due to blockage by large particles.

For a 45 μm screen size, ASTM E 11 allows average screen openings between 42 and 48 μm. In fact, 5% of the openings may be larger than 57 μm, while the largest opening allowed is 66 μm. Thus a careful screening performed with an ASTM specification screen may pass significant amounts of 45 to 57 μm material. The more careful and complete the screening, the more of this material passes through the screen and is incorrectly measured as −45 μm particles. On the other hand, as the amount of material on top of the screen increases, the difficulty of getting all the −45 μm material to pass through increases rapidly.

Screening can be a highly repeatable measurement, but the amount of skill required to produce good data is usually greatly underestimated. For fine, light material, wet screening is less subject to error than dry screening and is therefore specified here. The active flow of a liquid through the screen helps carry the fine solids through.

Safety Considerations:

1. Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.
2. Isopropyl alcohol — irritant to the skin and respiratory tract. Highly flammable.

Apparatus, Reagents, Materials:

1. Sieve — 325 mesh, i.e. 45 μm nominal diameter openings, meeting ASTM E 11 specifications for Wire-Cloth Sieves, 75 mm ID. Canadian Standard Sieve Series available from W.S. Tyler Co. of Canada Ltd., St. Catherines, Ontario, L2R 7B6. (1)
2. Centrifuge — 87 rev/s max., 4275 xG, 6 x 1000 mL capacity, complying with Class 1 Group D explosion-proof requirements, equipped with a six place horizontal head and 250 mL aluminum cups.
3. Beaker — 450 mL.
4. Funnel — polyethylene, 150 mm top diameter.
5. Oven — forced draft, set at 120°C.
6. Reagents:
   Toluene, A.C.S. reagent grade.
   Isopropyl Alcohol, A.C.S. reagent grade.
7. Analytical balance.
8. Desiccator.

Procedure:

1. Sample sizes shall be selected to yield 5 to 10 g of -45 μm particles.
2. Transfer the sample to a 250 mL centrifuge cup and fill to volume with a 50:50 toluene/isopropyl alcohol mixture. Mix thoroughly and centrifuge at 33 rev/s for 20 minutes. Carefully decant the extract, ensuring that no solids are lost. Replace the solvent mixture with toluene only and repeat the cleaning sequence until the decanted liquid is colorless. Fill the cup half full with isopropyl alcohol and set aside for the sieve analysis.
3. Heat the sieve and a 450 mL beaker for 30 minutes at 120°C. Cool in a desiccator and weigh to the nearest 0.1 mg. Nest the sieve in a large diameter funnel and support the assembly over the tared beaker.
4. Disperse the solids in the centrifuge cup by mixing with a spatula. Transfer the sample onto the sieve while gently tapping the sieve frame. Rinse the cup with isopropyl alcohol until the effluent entering the beaker is free of -45 μm particles. This is most easily checked by tipping the sieve and noting if particles flow down the inside rim.
5. When complete, remove the sieve from the funnel and dry for 2 hours at 120°C. Cool the sieve in a desiccator and reweigh.
6. Evaporate the sieve effluent to dryness in the oven and reweigh when cool.

Calculations:

$$\text{Weight \% (each fraction)} = \frac{w}{W} \times 100$$

where: w = weight of either fraction, g
W = sum of the weights of both fractions, g

Precision: As assessment of the precision for replicate -325 mesh particle size measurements on a typical middlings sample is reported below.

Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
54.64	± 1.93	3.53%

Data was obtained from 6 analytical sized samples obtained in rapid succession from a pilot plant process stream and hence includes sampling variability. It is expected that agreement among results would be highly dependent on sample preparation, operator skill in screening, and degree of sieve loading (sample size).

References:

1. ASTM. "Wire-Cloth Sieves for Testing Purposes." Annual Standards (1976), Part 41, Method E 11.

Determination of Particle Size Distribution by Sedimentation

Scope: This method determines the particle size distribution of −45 μm nominal diameter solids derived from process samples.

Summary: Dried −45 μm solids previously cleaned and segregated as in Method 4.1 are dispersed in a medium of known density and viscosity. The suspension is transferred to a Sedigraph 5000 Particle Size Analyzer and pumped through the cell assembly. When the flow is stopped, the Sedigraph 5000 determines, by means of a collimated beam of X-rays, the concentration of particles remaining at decreasing sedimentation depths as a function of time. The data is automatically presented as a cumulative percent fines distribution in terms of Stokesian or equivalent spherical diameter.

Background: For many years the standard method for determining the size distribution of fine particles has been based on the Stoke's Law equations, which predict the settling rate of a particle based upon the particle size and density, and the density and viscosity of the liquid medium in which the particles settle. One of the more popular of these methods involves suspending a sample in water, mixing it, then pipetting out a portion of the sample from a given depth, drying it, and weighing the residue to determine the solids concentration at the aliquot depth. Knowing the densities, viscosity, settling time, and depth from which the aliquot was taken, the maximum size in the sample can be calculated. Repeated application of this procedure to generate a particle size distribution is a time-consuming, tedious task.

It is well known that the attenuation of an X-ray beam is a measure of the density of the material the X-rays pass through. Many items of process equipment use this principle for industrial density measurement. Since the density of an aqueous suspension of solids is directly proportional to the solids content, it follows that with suitable calibration X-ray absorption would provide a direct measure of solids content at any point in the suspension. If this is done through the walls of a vessel within which a suspension is settling, measurements could be made to obtain exactly the same information as the pipet method without disturbing the system (1).

In essence the Sedigraph 5000 used in this method is based on the above principles. In practice it is provided with controls to set zero percent with clear water in the sample vessel and to set 100% with the sample maintained in suspension. The Sedigraph 5000 recorder then directly displays percent of the initial solids concentration remaining at a given depth. The horizontal pen movement of the recorder and depth of X-ray absorption measurement are simultaneously programmed so that the particle size indicated by the recorder pen position has settled from the top of the sample cell to the measuring beam. In this way results identical to the pipet method should be obtained more quickly and easily without the handling errors of the pipet method.

It must be emphasized that this measurement is not necessarily the true particle size but rather is the size of a spherical particle of the assumed density which would settle at the same rate as the measured particle. If the density is in error or if the shape is significantly non-spherical, significant errors can result. However, in all cases the measurement allows an accurate prediction of the settling properties of the solids.

Interferences:

1. The addition of even minute amounts of any solvent seriously interferes with the Sedigraph measurement.
2. Contamination of the cell with oil causes air bubbles to stick to the windows, producing erroneous results.
3. Flocculation of the samples produces erroneous results. Sodium metaphosphate is included in the dispersing medium to prevent flocculation.
4. As a general rule any increase in percent fines during a measurement indicates bubbles or flocculation. A drop below zero indicates a bubble at the top of the cell.

Safety Considerations: The Sedigraph 5000 produces X-rays when energized. Avoid exposure by keeping fingers away from the beam collimating posts. Operation in Alberta requires registration with the Radiation Protection Branch, Department of Labour.

Apparatus, Reagents, Materials:

1. Sedigraph 5000 Particle Size Analyzer. Micromeritics Instrument Corp., 5680 Goshen Springs Road, Norcross, GA 30093.
2. Waring Commercial Blender — two speed, equipped with Eberback semi-micro stainless steel container. Eberbach Corp., P.O. Box 1024, Ann Arbor, MI 48106.
3. Beaker — 50 mL.
4. Magnetic stirring bar.
5. Sodium Metaphosphate — purified.
6. Kodak Photo-flo 200 solution.
7. Volumetric flask — 1000 mL, Class A.
8. Top loading balance to ±0.001 g, 320 g capacity.
9. Distilled, deionized water.

Procedure: Preparation of Dispersion Medium

1. Prepare the dispersion medium by adding 0.5 g sodium metaphosphate and 5 mL Kodak Photo-flo 200 solution to one liter of distilled, deionized water.

Sample Preparation

2. Disperse approximately 1.1 g of dried −325 mesh solids, prepared by Method 4.1, in 25 mL of the dispersing medium by blending at low speed for 2 minutes. Proper instrument operation requires that the suspension be completely oil-free. Do not attempt to measure an oily samples.

Selection of Cell Movement Rate

3. In addition to particle size, sedimentation rate depends on the liquid viscosity and on the liquid and particle densities. The following calculations determine the rate of sample cell movement which correlates sedimentation rate with particle size for the solids/dispersing medium being investigated.

$$\text{Rate} = \frac{54.22\left(\rho-\rho_o\right)\left(\frac{60}{f}\right)}{\left(\frac{50}{D}\right)^2 \eta}$$

where: ρ = particle density, assumed to be 2.65 g/cc
ρ_o = liquid density, kg/L.
D = starting particle diameter, μm
η = liquid viscosity, mPa·s
f = line frequency, Hz

Densities and viscosities of the 1:200 Photo-flo in 0.05% sodium metaphosphate solution at various temperatures (a) are:

Temperature (°C)	Density (kg/L)	Viscosity (mPa·s)
26	0.9968	0.8737
28	0.9963	0.8360
29	0.9960	0.8180
30	0.9957	0.8007

Temperature (°C)	Density (kg/L)	Viscosity (mPa·s)
31	0.9954	0.7840
32	0.9951	0.7679
33	0.9947	0.7523
34	0.9944	0.7371
35	0.9941	0.7225
36	0.9937	0.7085
38	0.9930	0.6814

For a 50 μm starting diameter and 60 Hz line frequency (parameters usually employed for a sub 45 micron particle size distribution), this equation reduces to:

$$\text{Rate} = \frac{54.22\ (\rho-\rho_o)}{\eta}$$

Operating Procedure

4. Place a sheet of graph paper on the recorder plate. Set the RUN switch to RESET and then to the OFF position. Rotate the 100 PERCENT knob fully clockwise. Set the recorder pen to the 50 μm starting diameter.
5. Check the recorder reference baseline (0 percent on the graph) using the ZERO knob and ZERO push button. Flush and fill the sample cell with the Photo-flo/sodium metaphosphate solution and set the recorder to zero using the 0 PERCENT dial (b).
6. Load the dispersed sample into the sample cell. Add the stirring bar and set the stirring rate so that the solids remain suspended, but air is not drawn into the sample. Allow the sample to thermally equilibrate (a). Adjust the recorder to 100 percent.
7. Set the exact starting diameter and switch in the rate calculated in step 3 for the selected starting diameter. Remove the cell and inspect for bubbles. Replace the cell and recheck the starting diameter, 100 percent, and rate. Start the analysis by switching the RUN switch to ON.
8. After the analysis is completed the RUN switch is set to RESET and then returned to OFF. Clean and flush the cell. Leave the cell filled with clean dispersing medium when not in use.

Calculations: The chart obtained from the Sedigraph 5000 reads directly in cummulative % finer than versus equivalent spherical diameter (c).

Precision: Estimates for the precision of results have not been established. For a discussion of precision on a theoretical basis, consult the Sedigraph 5000 instruction manual.

Comments:

a. The cell compartment temperature should be approximately 6°C higher than the ambient temperature. The sample must be allowed to come to the same temperature as the cell compartment before initiating the run.

b. A scan of the cell using clean liquid should be done at least every second day to ensure that cell windows are parallel. The maximum deviation should be no greater than 1.5%.

c. Most samples dealt with are not made up of a single mineral. Other minerals may have different densities and are therefore incorrectly measured. Only the apparent equivalent spherical diameter, assuming a density of 2.65 g/cc, is obtained.

References:

1. Olivier, J.P., Hickin, G.K., and Orr, C. "Rapid Automatic Particle Size Analysis in the Subsieve Range," Powder Technology, 4, 257, (1970).
2. Micromeritics Instrument Corporation. Instruction Manual Sedigraph 5000 Particle Size Analyzer. Norcross GA, 1973.

Determination of Particle Size Distribution By Laser Diffraction

Scope: This method determines the particle size distribution of process stream samples including oil sand, reject, middlings, tailings, and dilution-centrifuging streams. Ashed solids may also be analyzed.

Summary: Samples are cleaned with an isopropyl alcohol and toluene mixture to remove the water and oil. The solids are dried and then riffled to obtain a sample size of 5 to 8 grams. The subsample is screened through a 100 mesh screen and the screened suspension is poured into a Microtrac particle size analyzer. This instrument uses laser diffraction to determine the particle size distribution of the -147 μm fraction.

Background: In the Microtrac particle size analyzer the sample is mixed with dilution water which is circulated continuously at a rate sufficient to keep the particles in random suspension. The light from a He-Ne laser is directed through a portion of the suspension to yield a diffraction pattern. The distribution of light in a horizontal plane from the normal beam target is measured and an internal computer uses this data to calculate the horizontal dimensions of the particles as they pass through the laser beam. The horizontal size is used to calculate spherical volume and yield an apparent volume percent distribution.

There are three significant limitations to the Microtrac. First, the diffraction pattern for particles below 1.9 μm cannot be properly measured. The sensitivity decreases rapidly from 1.9 to 1.0 μm. Below about 1.0 μm there is no sensitivity to the particles. Secondly, for particles larger than 250 μm, most of the diffraction pattern falls on the target used to block out the undiffracted laser beam. Thus the instrument is also blind to particles above 250 μm. The effective useful range is 1.9 to 176 μm. Thirdly, non-spherical particles are incorrectly measured. The extent of the error depends directly upon the probability of the various possible dimensions being measured. Both theoretical studies and direct measurements indicate that kaolin clays are overestimated by a factor of 3.7 in volume relative to spherical particles. This clay error is the major detrimental factor in the use of the Microtrac.

On the positive side, the laser diffraction instrumentation is easier to operate and maintain than other techniques. It also displays superb repeatability and is not operator sensitive.

Interference: The method measures all immiscible materials in the aqueous stream passed through the laser beam. Consequently oil droplets or air bubbles are measured as particles.

Safety Considerations:

1. Hydrochloric acid — highly toxic by inhalation. A strong irritant to the eyes and skin.
2. Isopropyl alcohol — irritant to the skin and respiratory tract. Highly flammable.
3. Laser — The main danger from the laser is in exposure of the eye to the laser beam, either directly or by reflection from a polished surface. The instrument employed here is equipped with an interlock designed to prevent any exposure of the user to the laser beam in normal operation.
4. Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.

Legal Requirements: In Alberta, all laser-based equipment is currently controlled under the Alberta Radiation Protection Act. The Occupational Health and Safety Division of the Alberta Department of Labour should be contacted for details. In particular, a responsible user must be identified for the instrument, and a Code of Practice developed. This Code of Practice must be read and signed by operators before the instrument is used.

Apparatus, Reagents, Materials:

1. Microtrac Particle Size Analyzer, Model 7991-02. Leeds and Northrup Co., M.D. 353, North Wales, PA 19454.
2. Sieve — 100 mesh, 147 μm nominal diameter openings.
3. Centrifuge — 87 rev/s max., 4275 x G, 6 x 1000 mL capacity, complying with Class 1 Group D explosion-proof requirements, equipped with 6 place pin type head and 250 mL aluminum cups.
4. Oven — forced draft, set at 110°C.
5. Ultrasonic probe — 400 W.
6. Riffler with pans — sixteen 3 mm chutes.
7. Sample bottles — 250 mL, linear polyethylene.
8. Reciprocating shaker — 40 mm stroke, set at approximately 5 cycles/s.
9. Beakers — 100, 250, and 600 mL.
10. Mortar and pestle — approximately 130 mm diameter, porcelain.
11. Sample jars — 125 and 250 mL.
12. Funnel — 150 mm top diameter.
13. Top loading balance to ±0.001 g, 320 g capacity.
14. Reagents:
    Hydrochloric acid, A.C.S. reagent grade.
    Isopropyl alcohol, A.C.S. reagent grade.
    Toluene, A.C.S. reagent grade.

Procedure:

Oil Sand and Core Sample Preparation

1. Transfer approximately 30 g of sample to a centrifuge cup. Fill the cup 2/3 full with 74% toluene/26% isopropyl alcohol (by volume) solvent blend and stir. Centrifuge for 10 minutes at 33 rev/s and decant the solvent. Repeat this cleaning sequence until the decanted solvent is clear. After the sample is cleaned, place the centrifuge cup in an oven set at 110°C to dry the sample. When the absence of solvent odor indicates the solids are dry, remove the centrifuge cup from the oven and cool. Proceed to the subsampling step (Step 6).

Middlings and Tailings Sample Preparation

2. Transfer the sample with isopropyl alcohol to a 250 mL jar and add 1.0 mL concentrated hydrochloric acid. Fill the jar 2/3 full with isopropyl alcohol. Cover and shake by hand for 5 seconds. Centrifuge for 10 minutes at 33 rev/s and decant the solvent. Add 150 mL of 74% toluene/26% isopropyl alcohol (by volume) solvent blend, cover, and shake for 5 minutes. Centrifuge for 20 minutes at 33 rev/s and decant the solvent. Repeat this cleaning step as needed until the decanted solvent is clear. Once the sample is clean, place the jar in an oven set at 110°C. When the absence of solvent odor indicates the solids are dry, remove from the oven and cool. Proceed to the subsampling step (Step 6).

Reject Sample Preparation

3. Place 5 to 8 g of dried hammermilled reject (Method 1.4) into a 250 mL jar and add about 150 mL of 74% toluene/26% isopropyl alcohol (by volume) solvent blend. Place the tip of the ultrasonic probe in the jar and adjust the power control to half maximum. Turn on the ultrasonic probe and rotate the power control to maximum power. Sonify for 10 seconds. Rinse the solids from the ultrasonic probe into the sample jar using isopropyl alcohol. Centrifuge for 10 minutes at 33 rev/s and then decant the solvent. Dry the sample in an oven set at 110°C before proceeding to the screening step (Step 7).

Ashed Solids Sample Preparation

4. No cleaning is required. Proceed directly to the screening step (Step 7).

Dilution-Centrifuging Sample Preparation

5. In preparing dilution-centrifuging samples care must be taken to ensure that the sample is not allowed to dry at any point during the procedure (a). Dilute the sample with an equal volume of 85% toluene/15% isopropyl alcohol (by volume) solvent blend and shake for 10 minutes. Transfer the sample to a 250 mL polyethylene bottle and immediately add some 74% toluene/26% isopropyl alcohol solvent blend (b). Fill to at least the 200 mL level with this blend.

   Shake for 5 minutes and then centrifuge for 20 minutes at 33 rev/s. Suction off the supernatant liquid, immediately add 74% toluene/26% isopropyl alcohol (by volume) solvent blend to the 200 mL level, and repeat the shaking and centrifuging. Proceed if the supernatant liquid is clear enough to see through to the bottom of the bottle. Otherwise continue the cleaning sequence.

   Suction off the supernatant liquid and immediately add about 200 mL of isopropyl alcohol. Shake for 5 minutes and centrifuge for 20 minutes at 33 rev/s. Suction off the supernatant liquid and immediately fill the bottle 3/4 full with water. Shake for 5 minutes. Proceed to the operating procedure (c) (Step 8).

Subsampling

6. Clean pans, riffler and mortar with compressed air and assemble the riffler and pans. Dump the cleaned dry solids into the mortar and gently break up the lumps using the pestle. Remove any rocks ($>$ 3mm) or extraneous material (wood, fiber, etc.) that is encountered. Pour the sample back into the sample container using a funnel. Then pour the contents of the sample container onto the center of the riffler. Tap the riffler until all the solids have dropped into the sample pans. Remove the pans and place a new set into position. Pour both of the riffled fractions into the riffler and tap through. Place the contents of one of the pans into a retain jar and continue splitting the contents of the other pan until the desired 5 to 8 g sample weight is obtained.

Screening

7. Weigh the subsample (to 0.001 g) into a 125 mL jar. Fill the jar approximately half full with isopropyl alcohol and sonify for 20 seconds as described previously. Screen the sample through a 100 mesh screen into a 600 mL beaker using hot water. Ensure all the lumps are broken up and washed through the screen. Save the wet -100 mesh portion for measurement.

   Wash the contents of the 100 mesh screen into a preweighed (to 0.001 g) beaker with water and dry at 110°C. Weigh when cooled to determine the weight of $+147$ μm solids.

Operating Procedure

8. Turn on the water supply and set all switches to initial settings:

Display/Print	1
Run	STEP
Set Zero	SET
Sample Time	200 s
Refill	AUTO
Sample Pump	AUTO
Rotator	ON
Computer	ON

Turn the POWER key switch to ON. Water should begin to fill the sample chamber. While the chamber is filling, check for a vacuum gauge reading of 50 to 65 kPa(a) (15 to 20 inches of mercury) and adjust the adjacent needle valve if necessary. Move the RUN switch to RESET and back to STEP. Let the unit warm up for at least 30 minutes. Press the POWER and REMOTE buttons on the printer.

Set Zero

9. Move the SAMPLE PUMP switch to OFF and clean the sample cell. Return the switch to the AUTO position. Push the DRAIN-RINSE button to drain and refill the sample chamber. Check that the SET ZERO switch is in the SET position and that the sample time is 200 seconds. Move the RUN switch from SET to RESET and then to RUN. Observe three cycles of logged data for background and as bubble checks. The background may be checked by observing the data from the second and third cycle. The raw data values must be less than 130 and may not vary by more than 002. If the data does not conform to these specifications repeat the set zero procedure.

   Move the SET ZERO switch to RUN, return the RUN switch to STEP and set the sample time to 400 seconds. The instrument is now ready for sample analysis.

   For the occasional zero check, move the DISPLAY/PRINT switch to 1, refill the chamber with fresh water and measure for 200 seconds after a 15 second debubble period. The display must not exceed $\pm$ 0.002 and the printed values must not exceed 010. If these conditions are not met, repeat the set zero procedure.

Sample Measurement

10. Select the proper display and printer mode (usually 6) on the DISPLAY/PRINT selector. Rinse and fill the sample chamber with water by pushing the DRAIN-RINSE button. While the chamber is filling, rinse the sample out of the beaker into it. After allowing at least one minute for the sample to disperse in the water, move the RUN switch from STEP to RUN and back to STEP. The red light above the switch will flash during the measurement and will be on continuously when the measurement is completed. The printer will automatically log the results. (d)

    After the analysis is completed push the DRAIN-RINSE button. The sample chamber will drain and then start to refill. When the water level has risen about 200 mm push the button again to start the rinse. Use a brush to clean the chamber if necessary. After at least 15 seconds push the button for a third time to drain and refill the chamber. Repeat the rinse, if necessary, by pushing the DRAIN-RINSE button again as the level rises. The instrument is now ready for another sample.

Calculations:

1. Calculate the percentage of + 147 μm material in the sample.

$$\%\ (+\ 147\ \mu m) = \frac{\text{Weight of Solids Retained in 100 Mesh Screen}}{\text{Sample Weight}} \times 100$$

2. Calculate the percentage of −147 μm material in the sample.

$$\%\ (-147\ \mu m) = 100 - \%\ (+147\ \mu m)$$

3. From the Microtrac data, the percentage of fines on a total sample basis is given by:

$$\%\ \text{finer (total)} = \frac{\%\ \text{finer (Microtrac)} \times \%\ (-147\ \mu m)}{100}$$

where: % finer (total) = weight percent of the total sample finer than a specified particle size.

% finer (Microtrac) = percentage of the −147 μm fraction of the sample determined as finer than a specified particle size by the Microtrac.

Precision: Strict precision evaluations to determine the repeatability of particle size measurements on a variety of process samples by laser diffraction have not been conducted. For diluted bitumen samples in particular, the agreement among results indicated below is considered typical. Data was generated from six analytical-sized samples collected in rapid succession from disc centrifuge feed.

Particle Size (μm)	Mean Value (wt% finer)	Standard Deviation (wt% finer)	Relative Standard Deviation
125	99.3	±0.8	0.8%
88	96.4	±2.6	2.7%
44	90.2	±3.0	3.3%
22	83.3	±2.6	3.1%
11	65.4	±1.6	2.4%
5.5	46.6	±0.8	1.7%
2.8	9.4	±0.4	4.3%

Comments:

a. The nature of dilution-centrifuging samples is completely different from other sample types described in this method. The final product in particular is difficult to redisperse if it is allowed to dry due to its very small average particle size.

b. Some dilution-centrifuging streams are low in solids. If desired several subsamples may be combined.

c. Some light-weight material, e.g. twigs, may come through the dilution centrifuging system. To protect the Microtrac pump and cell, the sample should be passed through a 100 mesh screen when being placed in the Microtrac.

d. After 15 minutes air becomes entrained in the water and will cause the larger particle size fractions to have high values. Therefore, do not make any measurements when the water is more than 15 minutes old.

References:

1. Weiss, E.L. and Frock, H.N. "Rapid Analysis of Particle Size Distribution by Laser Light Diffraction." Powder Technology, 14, 287 (1976).

2. Cornillault, J. "Particle Size Analyzer" Applied Optics, 11, 265 (1972).

3. Leeds and Northrup. 7991-02 Microtrac Particle Analyzer. North Wales, PA, 1977.

CHAPTER 5

ANALYSIS OF BITUMEN AND DERIVED HYDROCARBONS

The conversion of bitumen to synthetic crude is the beginning of a sequence that continues in a refinery. Consequently, analytical methods developed by ASTM (Committee D-2 on Petroleum Products and Lubricants), Universal Oil Products, or the Institute of Petroleum are often useful in bitumen upgrading (1-4).

Hydrocarbon type and distillation properties are two major characterizations for petroleum hydrocarbons. For bitumen the separation into saturate, aromatic, resin, and asphaltene (SARA) fractions is described in Method 5.1. In Method 5.2, a 40 theoretical plate spinning band vacuum distillation apparatus which permits the collection of fractions up to an atmospheric equivalent temperature of 525°C or the onset of cracking is presented. These two methods are grouped together under the heading of separation techniques, since they provide fractions for analysis by other procedures in addition to yields according to hydrocarbon type or boiling point.

In the petroleum industry, numerous analyses are known that give separation data but are not intended to yield fractions for subsequent analysis. These permit characterization by hydrocarbon type or distillation properties without the tedium of collecting fractions. For example, hydrocarbons distilling below 315°C may be analyzed by the fluorescence indicator adsorption (FIA) method described in ASTM D 1319. This analysis determines saturate, nonaromatic olefin and aromatic hydrocarbon types. In UOP Method 501 the FIA technique is applied to samples boiling in the range 150-400°C. Another variant of hydrocarbon type characterization is the paraffin, olefin, naphthene, and aromatic (PONA) analysis described by UOP Method 273. Recent trends in hydrocarbon type analysis are based on high performance liquid chromatography, although spectroscopic techniques such as nuclear magnetic resonance and mass spectroscopy are also developing rapidly.

The distillation properties of bitumen or derived hydrocarbons may also be determined without the tedium of collecting fractions from a distillation. For volatile hydrocarbons, i.e. final boiling point less that 525°C, simulated distillation by gas chromatography using ASTM D 2887 enjoys widespread use and is commercially available as a turn-key analysis. Recently ASTM has extended the scope of this analysis to samples containing non-volatile material. The proposed ASTM method (5) uses a standard addition to determine the amount of volatile material in the sample. Method 5.3 includes a further modification by incorporating distillation cuts from Method 5.2 to determine relative response factors for improved quantitation.

The Conradson and Ramsbottom carbon residues both provide information about the coking properties of samples. Like many procedures, the tests are significant when the data is compared to an existing body of data and correlations. Thus the Conradson procedure modified with an ash correction (Method 5.4) is used by Syncrude Research to allow comparison of bitumen coking tendencies with data from other sample types characterized by Conradson carbon residue.

In Method 5.5 a pycnometer method for the determination of bitumen density is presented. The method is required for very viscous samples which are not easily transferred with a syringe. The density provided by the pycnometer method permits completion of the calculations required for the spinning band distillation of bitumen and for the determination of API gravity. If the sample may be handled with a syringe, Method 3.6 is preferred.

Method 5.6 provides for the determination of the number average molecular weight of bitumen and bitumen fractions by freezing point depression. This procedure and Method 5.1 for SARA analysis include the use of benzene as a reagent. The methods are presented to describe the standard practice of Syncrude Research when last used. In view of the toxic nature of benzene (6) the substitution of alternative solvents would now be recommended.

In Method 5.7 for the determination of bromine number, 1,1,1-trichloroethane replaces the carbon tetrachloride employed by ASTM and UOP. Carbon tetrachloride is highly toxic and is particularly linked to liver damage. By comparison, 1,1,1-trichloroethane has a much higher threshold limit value. The method also incorporates automation which reduces the operator time from 1 hour to about 15 minutes.

Raw bitumen is high in sulfur and nitrogen and one aim of upgrading is to reduce the levels of these elements. Numerous ASTM methods are available for these analyses. For example the quartz-tube method, ASTM D 1551, and induction furnace with iodometric titration of sulfur dioxide, ASTM D 1552, have historically been used by Syncrude Research for the analysis of sulfur in bitumen. The equipment required for these methods is inexpensive and the time per analysis is about 30 minutes. However, as a result of the research effort for alternative energy sources being directed towards high sulfur materials such as coal, coke, and heavy oils, a new generation of microprocessor-based instrumentation for sulfur analysis is becoming available (7). For more ideal samples such as distillation cuts or upgrading streams, determinations of sulfur by dedicated nondispersive X-ray fluorescence (Method 5.8) and by oxidative microcoulometry (Method 5.9) are included in this collection. The dedicated X-ray fluorescence method provides an ideal analysis for samples which are homogeneous and easily poured. The method, however, lacks the sensitivity displayed by oxidative microcoulometry.

The determination of total nitrogen in liquid petroleum hydrocarbons by chemiluminescence is described in Method 5.10. The method is particularly interesting for two reasons. First, the chemiluminescent procedure is a sufficiently recent development that no standard methods are available in the literature for this technique. Secondly, this method is a model that might suggest other applications where the speed, ease of use, and exceptional sensitivity of the chemiluminescent nitrogen technique are desired.

Bitumen contains nickel, iron, and vanadium at the several hundred part per million level. Analysis for these metals during upgrading is required, since they are known poisoners of cracking catalysts. Method 5.11 is based on inductively coupled argon plasma which has detection limits superior to X-ray fluorescence.

References

1. ASTM Committee D-2. Manual on Hydrocarbon Analysis. Third Edition, 1977.
2. ASTM Committee D-2. Significance of Tests for Petroleum Products. ASTM Special Technical Publication 7C, 1977.
3. Universal Oil Products. UOP Laboratory Test Methods for Petroleum and Its Products. Universal Oil Product Process Division, Des Plaines, IL.
4. The Institute of Petroleum. IP Standards for Petroleum and Its Products. 32nd Edition, Applied Science Publishers Ltd., 1973.
5. ASTM Committee D-2. "Proposed Test Method for Boiling Range Distribution by Gas Chromatography". Annual Standards (1976), Part 25, pp. 716-722.
6. Occupational Safety and Health Administration. Standard for Occupational Exposure to Benzene. January, 1978, (NTIS PB-278295).
7. For example the Fisher Model 475 and Leco Model SC-32 sulfur analyzers.

Analysis for Saturates, Aromatics, Resins and Asphaltenes in Bitumen by Liquid-Solid Chromatography

Scope: This method separates and determines the saturate, aromatic, resin and asphaltene fractions within bitumen.

Summary: A sample of bitumen is dissolved in an equal volume of benzene. Forty volumes of n-pentane are added for each volume of benzene. The resulting precipitate is collected by filtration and weighed as asphaltenes. The filtrate is refluxed on a recycle adsorption apparatus packed with Attapulgus clay. Resins adsorb on the Attapulgus clay while the saturates and aromatics are carried to the kettle. The resins are eluted from the Attapulgus clay with methyl ethyl ketone and tetrahydrofuran containing 5% water by volume. Separation of the saturates and aromatics is performed on a chromatographic column packed with alumina and silica gel. The saturates and aromatics are eluted with n-pentane and benzene respectively. Any resin which may have remained is eluted with methyl ethyl ketone. All fractions are determined gravimetrically after evaporation of the solvent.

Background: The fractions denoted as saturates, aromatics, resins and asphaltenes in this procedure are defined operationally by the specific test conditions described in the method. The fractions are not clean-cut separations according to molecular type. Instead, they represent a separation based on solubility and strength of adsorption and must be identified with the procedure by which they are generated. This operational definition of the fractions is emphasized since similar terminology for designating fractions is employed by methods using different separation conditions.

In practice the separation is reproducible and hence useful for evaluating similarities and differences among different bitumen samples.

The asphaltenes are attributed to condensed aromatic ring systems with high nitrogen, sulfur, oxygen, and metal contents. On the other hand, the saturate and aromatic fractions contain very little sulfur, nitrogen, or metals. The sulfur and nitrogen which is present is embedded in large nonpolar molecules so that a very low affinity for activated clays occurs. The resin fraction is obtained almost as a remainder, and is attributed to molecules which contain actively available polar groups, but which do not precipitate in the asphaltene fraction.

Safety Considerations:

1. Benzene — highly toxic and a suspected carcinogen. Employ strict precautions to prevent inhalation and skin absorption.
2. Methyl ethyl ketone — moderately toxic by inhalation and skin absorption. Extremely flammable.
3. Pentane — extremely flammable.
4. Tetrahydrofuran — highly toxic by inhalation and skin absorption. Extremely flammable. Since tetrahydrofuran may form explosive peroxides, verify the absence of peroxides prior to use. In this experiment water is added to the tetrahydrofuran. Never reflux the tetrahydrofuran in the absence of this water.

Apparatus, Reagents, Materials:

1. Recycle Adsorption Apparatus — shown in Figure 1 and consisting of:
   - i) Kettle — round bottom, two neck heat-resistant flask with 28/15 socket joints, 500 mL capacity.
   - ii) Chromatographic column with insulating jacket — 22 x 450 mm, 35/25 socket joint at the top and 28/15 ball joint at the bottom.
   - iii) Distilling tube — 10 x 450 mm with 28/15 ball and socket joints.
   - iv) Condenser — with drip tip and 35/25 ball joint, equipped with a side arm downcomer having a 28/15 ball joint to accommodate the distilling tube.
   - v) Pinch clamps — size No. 28 and No. 35.
   - vi) Variable transformer — 0 to 280 V to control heating mantle.

vii) Heating mantle — hemispherical for 500 mL flask.

viii) Ball joint — 35/25 joint with hose adapter for nitrogen purge.

2. Chromatographic column — 16 x 900 mm with 12 mm tapered outlet. The upper end of the tube is fitted with a 12/30 standard taper joint for connection to a 250 mL reservoir funnel.
3. Filter funnel — 150 mL Buchner type with medium pore fritted glass filter. A filtering flask under slight vacuum is required for use with the filtering crucible.
4. Evaporating dish — 250 or 500 mL capacity.
5. Erlenmeyer flask — 300 mL.
6. Rotary evaporator with 500 mL evaporating and receiving flasks.
7. Steam bath.
8. Nitrogen.
9. Oven — forced draft, set at 105°C.
10. Solvents:
    Benzene, A.C.S. reagent grade
    Methyl ethyl ketone, A.C.S. reagent grade
    n-Pentane, conforming to the requirements of ASTM D 893
    Tetrahydrofuran, histological grade, 5% water added by volume
11. Adsorbents:
    Alumina, grade F-20, 80-100 mesh. Aluminum Company of America
    Attapulgus clay, grade AA.LVM, 30-60 mesh. Engelhard Minerals and Chemical Corporation
    Silica gel, code 923, 100-200 mesh. Davison Chemical Co.

    All adsorbents are activated at 150°C for 3 hours and stored in dry sealed containers before use.
12. Analytical balance.

Procedure:

1. Accurately weigh 2.5 g of bitumen sample into a 300 mL Erlenmeyer flask tared to 0.1 mg. Correct this weight for residual benzene or toluene content if applicable (a). Dissolve the sample in a volume of benzene (mL) numerically equal to the sample weight in grams, warming only if necessary. When fully dissolved, slowly introduce 40 mL of n-pentane for each mL benzene previously added. Stopper and shake the flask thoroughly for 5 minutes. Allow the precipitate to settle in subdued light for 2 hours, with occasional shaking.
2. Filter the suspension through a filtering funnel, tared to 0.1 mg, into a filtering flask under slight vacuum. Rinse the flask with n-pentane and transfer the washings to the filtering funnel. Wash the precipitate until the effluent is colorless. Dry the filtering funnel and original flask which contains a small amount of precipitate adhering to the walls at 105°C. Reweigh and record the weight increase as ASPHALTENES.
3. Evaporate the filtrate to approximately 10 mL in a 500 mL round bottom flask on a rotary evaporator.
4. Pack the chromatographic column of the recycle adsorption apparatus with glass wool in the lower 25 mm. Pack the remaining column with Attapulgus clay, tapping the column throughout until a depth of approximately 300 mm is obtained.
5. Assemble the recycle adsorption apparatus with the kettle containing 150 mL of n-pentane. Prewet the column with 50 mL of n-pentane. Transfer the filtrate from Step 3 to the column using n-pentane as a wash. Reflux for two hours. Allow the column to drain and then purge with nitrogen until the clay is dry. Remove the kettle, now containing saturate and aromatic fractions, and reduce the volume of solvent to approximately 5 mL. Save for separation under Step 9.

6. Elute RESINS I adsorbed on the clay by refluxing with 200 mL of methyl ethyl ketone for one hour. Allow the column to drain and then purge with nitrogen until the clay is dry. (b)
7. Transfer the methyl ethyl ketone solution to an evaporating dish, tared to 0.1 mg, and evaporate to dryness on a steam bath to remove the solvent. Place the dish in an oven at 105°C for 5 minutes. Cool in a desiccator, weigh, and record the weight increase as RESINS I.
8. Similarily, elute the RESINS II adsorbed on the clay by refluxing with 200 mL of tetrahydrofuran containing 5% water by volume for one hour. Determine the quantity of RESINS II as outlined in Step 7.
9. Pack a 16 x 900 mm chromatographic column with 30 mm of alumina over 650 mm of silica gel. Prewet the column with n-pentane and transfer the mixture of saturates and aromatics from Step 5 to the column. When the last drops of the solution are just entering the alumina, commence the addition of 200 mL of n-pentane.
10. When the last drops of n-pentane are entering the alumina start the addition of 120 mL of benzene.
11. Collect the pentane effluent in an evaporating dish tared to 0.1 mg. Continue collection of this fraction until the benzene front is 75 to 100 mm from the bottom of the column. Evaporate to dryness as in Step 7 and weigh the residue as SATURATES.
12. When the last drops of benzene are entering the alumina, begin addition of 120 mL methyl ethyl ketone. Collect the benzene effluent in an evaporating dish tared to 0.1 mg, until the methyl ethyl ketone front is 75 to 100 mm from the bottom of the column. Evaporate the solvent and weigh the residue as AROMATICS.
13. Similarily, collect the methyl ethyl ketone fraction until the effluent becomes colorless. Evaporate to dryness and weigh. Add this residue weight to that obtained in Step 7 to arrive at total RESINS I content.

Calculations: Calculate the weight percent of each fraction.

$$\text{Wt \%} = \frac{w}{W} \times 100$$

where: w = weight of each fraction, g
W = weight of sample, g

Precision: The following data based on 6 determinations illustrates the typical precision associated with a SARA analysis for a bitumen sample.

	Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
Asphaltenes	17.18	±0.19	1.11%
Resins I	38.99	±0.77	1.97%
Resins II	5.85	±0.25	4.27%
Saturates	16.87	±0.10	0.59%
Aromatics	18.27	±0.58	3.17%
Overall Recovery	97.16	±0.82	0.84%

Comments:

a. The determination of residual benzene and toluene are described in Methods 3.2 and 2.7 respectively.

b. If the methyl ethyl ketone eluate is to be subjected to further analysis, it should be realized that a small quantity of ketol is formed and remains in the sample. Not all the methyl ethyl ketone is removed by normal drying procedures.

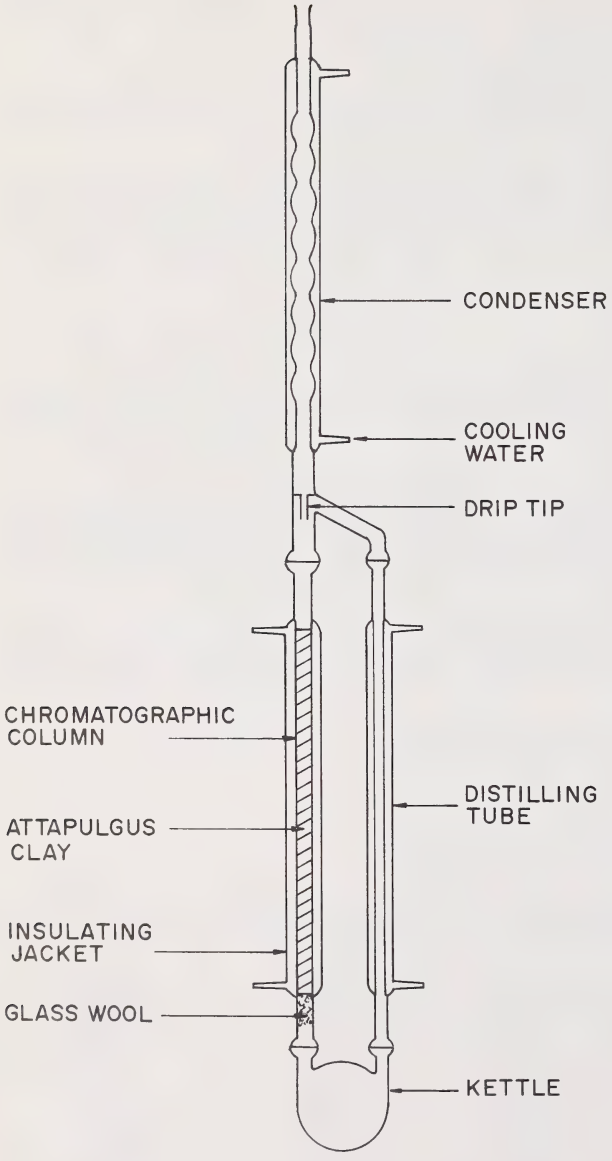


FIGURE 1: RECYCLE ADSORPTION APPARATUS

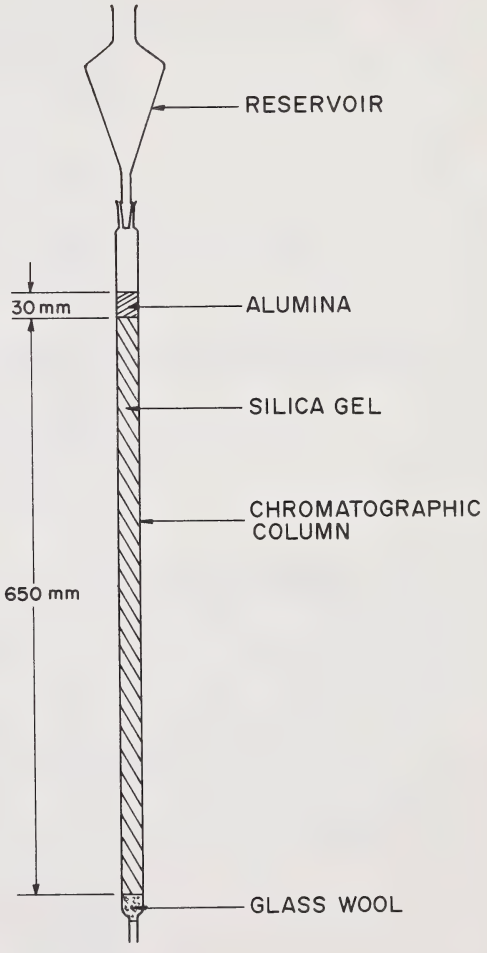


FIGURE 2: CHROMATOGRAPHIC COLUMN

Spinning Band Distillation of Liquid Hydrocarbons and Bitumen

Scope: The samples covered by this method include liquid hydrocarbon and bitumen samples. For liquid hydrocarbons, the initial boiling point of the sample should exceed room temperature at atmospheric pressure. The distillation is terminated at an atmospheric equivalent temperature of 524°C. For bitumen samples the distillation is terminated at a pot temperature of 360°C.

Summary: Samples are distilled under atmospheric and reduced pressures of 2.67 kPa(a) and 80 Pa(a) (20.0 and 0.60 mm Hg) in a distillation unit equipped with a spinning band column. The spinning band, which effectively provides a large contact area between the liquid and vapour phases, increases the number of theoretical plates in the column and thus its fractionating efficiency. Readings of vapour temperature, which is convertible to atmospheric equivalent temperature, and distillate volume, which is convertible to volume percent, are used to plot a distillation curve. Distillate yields for naphtha, light gas oil, heavy gas oil and residue fractions are determined on a gravimetric basis.

Background: Distillation is one of the simplest methods to separate the complex mixtures in petroleum samples. ASTM and UOP include several types of distillation for application to diverse sample materials:

ASTM D 86	Distillation of Petroleum Products
ASTM D 216	Distillation of Natural Gasoline
ASTM D 285	Distillation of Crude Petroleum
ASTM D 1160	Distillation of Petroleum Products at Reduced Pressure
ASTM D 2892	Distillation of Crude Petroleum (15 Theoretical Plate Column)
UOP 1	Distillation of Heavy Petroleum Oils
UOP 76	High-Vacuum Distillation of High Boiling Range Petroleum Products
UOP 77	Crude Oil Evaluation by Hempel Distillation
UOP 79	Fractionation of Petroleum Distillates and Crude Oils
UOP 109	Vacuum Distillation of Topped Crude Oils and Similar Petroleum Products

The present method employs a rotating metal band inside the distillation column. The principles and advantages of the spinning band are documented elsewhere (1). Using this method samples can be distilled under atmospheric or reduced pressure. For each twofold pressure reduction the boiling point of most compounds is lowered by approximately 15°C. Some components present in bitumen are thermally unstable and crack at temperatures below their boiling points. To avoid cracking, the pressure is reduced during the distillation. However, due to the pressure drop between the still head and the McLeod gauge, the lowest pressure used in this procedure is 80 Pa(a) (0.6 mm Hg). This corresponds to an atmospheric equivalent temperature (AET) of approximately 500°C for bitumen samples.

The samples are distilled into a number of fractions so that further analyses can be performed on the cuts. The designations and boiling point ranges employed are:

Naphtha	IBP - 195°C
Light Gas Oil	195 - 343°C
Heavy Gas Oil	343 - 524°C
Residue	>524°C

where: IBP is the initial boiling point.

The Sydney Young equation is used to relate vapour temperature to atmospheric equivalent temperature (AET) for distillation at atmospheric pressure (2). For distillation at reduced pressure, an equation based on the data of Maxwell and Bonnell are used (3,4). The effect of hydrocarbon type (5), as measured by the UOP characterization factor, K, is included in the latter calculation. A value for this factor of 12.5 or higher indicate a material predominately paraffinic in nature, whereas highly aromatic materials have a value of 10 or less. The calculations for this method employ a K-factor of 11.1, which has been found suitable for Athabasca bitumen.

Interferences:

Water contained by liquid hydrocarbon samples in either dispersed or coalesced form will cause severe bumping during the distillation. Solids present in a sample will report to the residue fraction and consequently bias distillate yields. Consequently, most of the water and solids must be removed as outlined in the sample preparation step of this procedure.

Safety Considerations:

1. Dry ice — freezes skin, wear protective gloves.
2. Liquid nitrogen — freezes skin, wear protective gloves.
3. Isopropyl alcohol — irritant to the skin and respiratory tract. Highly flammable.
4. Toluene — moderately toxic by skin absorption and inhalation. Possesses irritant and anesthetic properties. Highly flammable.
5. Glassware under reduced pressure is capable of violent implosion. Break vacuum with extreme caution.
6. Do not use liquid nitrogen in the dry ice traps.

Apparatus, Reagents, Materials:

1. Adiabatic metal mesh spinning band still — 480 mm x 7 mm ID column, 40 theoretical plates, 0.3 mL hold-up, vacuum capability to 4.0 Pa(a) (0.03 mm Hg), monel band, 29 rev/s motor and direct drive system. Perkin-Elmer order number 086-0901. The manual reflux valve assembly is replaced by the auto-reflux valve assembly. Perkin-Elmer order numbers 086-0215 and 086-0213.
2. Still pots — 500 mL for liquid hydrocarbon samples, 200 mL for bitumen samples, 50 mL for still hold-up. Single neck, round bottom flasks to fit the column and equipped with thermocouple well. Perkin-Elmer order numbers 086-0916, 086-0232, and 086-0230 respectively. Rubber stoppers to fit above flasks are also required.
3. Fraction cutter and supply of 25 mL capacity receivers. Perkin-Elmer order numbers 086-0313 and 086-0314 respectively. Glass stoppers to fit the receivers are also required.
4. Vacuum gauge — Universal 3-scale McLeod type, portable, VWR No. 31704-008, Western Scientific Services Ltd., 2520 Simpson Road, Richmond, B.C. V6X 2P9.
5. Heating mantle — 270 W, to fit 500 mL and 200 mL round bottom flasks. Top heating mantles, 170 W, to fit the flasks.
6. Heating tape — 8 x 300 mm. The heating tape supplied as part number 519663 by Dohrmann Division of Envirotech Corp., 3240 Scott Boulevard, Santa Clara CA 95050 is suitable.
7. Variable transformers for heating mantles and heating tape.
8. Magnetic stirrer with bar.
9. Indicator control panel equipped with multipoint temperature selector, digital temperature indicator and reflux timer. The timer requires a minimum ON or OFF setting of 1 second. The Flexopulse Model HG92 supplied by Eagle Signal, 736 Federal, Davenport, IA 52803 is suitable.
10. Two vacuum pumps and tubing — the primary vacuum pump requires 8.3 L/s free air capacity.

11. Pinch clamp — no. 28.
12. Surge tank, manifold, mineral oil trap, dry ice traps, and needle valve as illustrated schematically in Figures 1 to 3.
13. Centrifuge — 87 rev/s max., 4275 x G, 6 x 1000 mL capacity, complying with class 1 Group D explosion-proof requirements, equipped with a six place horizontal head and 250 mL aluminum cups.
14. Balances:
    Top loading to 0.001 g, 320 g capacity
    Top loading to 0.01 g, 1200 g capacity.
15. Barometer — U.S. Signal Corps type.
16. Dewar flask — 10 L, for liquid nitrogen.
17. Evaporating dish — 120 mL, porcelain.
18. Separatory funnel — 500 mL.
19. Apiezon T grease.
20. Reagents:
    Dry ice
    Isopropyl alcohol, A.C.S. reagent grade
    Liquid nitrogen
    Mineral oil
    Nitrogen gas
    Toluene, A.C.S. reagent grade.
21. Molecular sieves — type 4A.

Procedure: Sample Preparation — Liquid Hydrocarbon Samples

1. Liquid hydrocarbon samples may contain water. Centrifuge these samples at 33 rev/s for 30 minutes to separate the major portion of the water from the hydrocarbon phase. Carefully withdraw the hydrocarbon phase by means of a syringe and transfer to a 500 mL separatory funnel containing approximately 60 g of molecular sieve. Allow to stand overnight.
2. Weigh the still pot containing a magnetic stirring bar and fitted with a rubber stopper on a top loading balance to the nearest 0.01 g. Discarding the first few drops which may contain water, collect approximately 100 mL of sample in the still pot. Stopper and reweigh. Take a small portion of the sample remaining in the separatory funnel and determine its density at 20°C using Method 3.6.

Sample Preparation — Bitumen Samples

3. Heavy bitumen type materials must be rendered less viscous so they can be sampled. Loosen the cap of the sample container. Place the sample container in hot water (70 to 90°C) and allow the sample to warm until the sample is fluid enough to be stirred easily with a rod. Stir thoroughly to distribute any solids present.
4. On the top loading balance weigh to the nearest 0.01 g the still pot containing a magnetic stirring bar and fitted with a rubber stopper. Transfer approximately 100 grams of the sample to the still pot. Stopper and reweigh. Take a small portion of the sample remaining in the sample container and determine its density at 20°C using Method 5.5

Preparation of Distillation Apparatus

5. Half fill the dry ice traps (see Figure 3) with isopropyl alcohol. Carefully add dry ice to the liquid in each vessel, a few pieces at a time at first to prevent the mixture from bubbling over, and then more liberally as the mixture cools. Ultimately each vessel should be filled to within 20 to 30 mm of the top. Since it will take some time to cool these vessels, it is advantageous to begin this step as soon as possible. As the run proceeds, dry ice will sublime and more should be added as replacement.

6. Label and weigh several fraction receivers and corresponding glass stoppers to the nearest 0.001 g.

7. Apply Apiezon T grease sparingly to all ground glass joints and the O-ring at the bottom of the distillation column (see Figure 2). Connect the still pot, fraction cutter and receivers to the distillation assembly. Rotate glassware about the joints to ensure a good seal. Position the receivers to ensure their graduations are visible to the operator. Use small springs to formally attach the still pot to the column and the receivers to the fraction cutter. Insert the thermocouple into the still pot well and ensure that the thermocouple in the still head is secure. Turn on the water to the condenser.

Atmospheric Distillation

For samples containing naphtha, IBP-195°C, an atmospheric distillation is performed. For samples such as bitumen containing little or no naphtha proceed to the vacuum distillation in step 17.

8. Set the reflux timer to provide a reflux ratio of 20:1 by setting the closed period for the reflux valve to 20 seconds and the open period to one second. Depending on the sample type, the reflux ratio may have to be adjusted. If the vapour temperature drops after a portion of distillate has been removed or if the condensation rate decreases, then the reflux ratio must be increased. Conversely, if the rate of condensation is very fast then the reflux ratio should be decreased.

9. Ensure that all stopcocks associated with the vacuum system are positioned as indicated in Figure 3. It is imperative that stopcocks D and I be open to the atmosphere. Attempting to do a distillation in a closed system will result in a pressure increase inside the still and possible explosion. To prevent vapours entering the McLeod gauge, ensure that stopcock H is closed.

10. Raise the heating mantle to surround the bottom half of the still pot.

    Switch on the digital temperature monitor and magnetic stirrer. Set the variable transformer supply to the bottom heating mantle to 70 V and switch it on to initiate the heating. Activate the spinning band when the vapour temperature starts to rise, indicating sufficient liquid in the column to lubricate the band. Caution should be exercised during the beginning of the distillation as any water present in the sample may cause it to bump. Until this possibility is past (e.g. vapour temperature greater than 100°C) monitor the still pot closely and lower the heating mantle if bumping occurs. When there is no further potential for bumping, place the top heating mantle over the still pot.

Naphtha Fraction

11. Obtain the atmospheric pressure reading in the laboratory from a barometer. Obtain the initial boiling point (IBP) of the sample by observing, through the reflux window, the drop point at the bottom of the condenser. The IBP is the vapour temperature at which the first drop falls. A second drop should immediately begin to form. Record the IBP as displayed on the digital temperature monitor.

12. When a condensation rate of about 2 drops/second has been established, switch on the reflux timer and immediately record the vapour temperature corresponding to a volume of 0 mL. Activating the reflux timer will cause 1 part of condensate to be diverted to the fraction cutter and receiver and 20 parts to return to the column. If the rate falls below 2 drops/second, the reflux timer should be shut down until this equilibrium position is again achieved. It may be necessary to increase the time that the reflux valve is closed. It is important that the condensate drops into the center of the bend of the fraction cutter and into the center of the graduated receiver. Adjust glassware as necessary.

13. If the sample is heated too quickly at atmospheric pressure or particularly at the lower pressure used in this distillation, excess liquid can be forced up the still into the condenser. This is termed flooding. The first indication of flooding is a flickering at the top of the column observed through the reflux window. If this

occurs, switch off the reflux timer, lower the heating mantle, and turn down the variable transformer for the heating mantle slightly. When the flooding has subsided, raise the heating mantle and continue the distillation. Turn on the reflux timer when a condensation rate of 2 drops/second is achieved.

14. Record the vapour temperature for every mL condensate collected. Record the pot temperature at 5 mL intervals.

    It is not uncommon that a minor amount of residual water in the sample charge will distill with the naphtha and settle in the receiver. If the estimated amount of water collected exceeds 0.1 mL, record the volume and apply necessary corrections for calculating weight % distillate yields (see Calculations).

15. Continue the distillation until the vapour temperature corresponds to 195°C AET. Consult table below. Should the receiver fill to the 25 mL mark before reaching this temperature, rotate the fraction cutter to present a new receiver for incoming distillate.

Pressure		Vapour Temperature
kPa(a)	mm Hg	°C
88.1 to 90.5	661 to 679	190
90.5 to 92.9	679 to 697	191
92.9 to 95.3	697 to 715	192
95.3 to 97.7	715 to 733	193

16. Switch off the reflux timer, variable transformer for the bottom heating mantle, and magnetic stirrer in that order and immediately lower the heating mantle. Allow the fraction cutter to drain and rotate to position a new receiver. Remove and stopper the filled receiver(s) and reweigh to the nearest 0.001 g. Replace with clean, weighed receiver(s).

Vacuum Distillation

17. The distillation assembly is equipped with two vacuum pumps; a primary pump to evacuate the still and a secondary pump for operating the McLeod gauge. Before starting evacuation procedures, ensure that stopcock B is open to the atmosphere, that stopcock C is open between the gauge and mercury reservoir (closed to mercury trap) as indicated in Figure 4 (a). Open stopcock H and close stopcocks D and I (Figure 3). Turn on the secondary vacuum pump, and after it has started to draw a vacuum activate the primary vacuum pump. Adjust needle valve A (Figure 1) on the bleed line until a pressure of 2.67 $\pm$0.07 kPa(a) (20.0 $\pm$0.5 mm Hg) is achieved. Referring to Figure 4 (b), obtain a pressure reading in the McLeod gauge as follows:

    i) turn stopcock C slowly to connect the mercury reservoir to the mercury trap

    ii) when the mercury rises to the first zero marking on the scale, close stopcock C to all lines

    iii) read pressure as indicated on right hand scale.

    Evacuate the gauge as instructed below and illustrated in Figure 4 (d):

    i) turn stopcock B to connect the secondary vacuum line and the mercury trap

    ii) when a vacuum is achieved, turn stopcock C to connect the mercury reservoir to the trap

    iii) when all mercury returns to the reservoir, rotate stopcock C to connect the gauge and reservoir, and stopcock B to connect the atmosphere and mercury trap (as illustrated in Figure 4 (a)).

    If the observed pressure reading deviates from 2.67 $\pm$ 0.07 kPa(a) (20.0 $\pm$ 0.5 mm Hg), adjust the bleed valve, wait for equilibrium and repeat the pressure measurement and gauge evacuation procedures.

18. Raise the heating mantle to surround the bottom half of the still pot. Switch on the temperature monitor and the magnetic stirrer. Bitumen samples may be too viscous to stir until the pot temperature reaches approximately 100°C.

Set the variable transformer for the bottom heating mantle to 70V and switch it on to initiate the heating. Activate the spinning band when the vapour temperature starts to rise, indicating sufficient liquid in the column to lubricate the band. Again, caution should be exercised during the beginning of the distillation as any water present in the sample may cause it to bump. Until this possibility is past monitor the still pot closely and lower the heating mantle if bumping occurs. When there is no further potential for bumping, place the top heating mantle over the still pot.

Light Gas Oil Fraction

19. For bitumen samples or samples containing no naphtha fraction, obtain the initial boiling point (IBP) of the sample by observing, through the reflux window, the dropping point at the bottom of the condenser. The IBP is the vapour temperature at which the first drop falls. A second drop should immediately begin to form. Record the IBP as displayed on the digital temperature monitor.

20. When the condensation rate of about 2 drops/second has been established, switch on the reflux timer, set at a reflux ratio of 3:1 (see step 8) and immediately record the vapour temperature corresponding to a volume of 0 mL. Activating the reflux timer will cause 1 part of condensate to be diverted to the fraction cutter and receiver and 3 parts to return to the column. If the rate falls below 2 drops/second, the reflux timer should be shut down until this equilibrium position is again achieved. The reflux ratio may need to be adjusted. It is important that the condensate drops into the center of the bend of the fraction cutter and into the center of the graduated receiver. Adjust glassware as necessary.

    If the sample is heated too quickly at the low pressures used in this distillation, flooding may occur. The first indication of flooding is a flickering at the top of the column observed through the reflux window. If this occurs, switch off the reflux timer, lower the heating mantle, and turn down the variable transformer for the bottom heating mantle slightly. When the flooding has subsided, raise the mantle and continue the distillation. Turn on the reflux timer when a condensation rate of 2 drops/second is achieved.

21. Record the vapour temperature for every mL of condensate collected. Record pot temperature at 5 mL intervals. Monitor and record system pressure several times during the distillation.

22. Some bitumen samples may contain a small amount of naphtha, i.e. components with bp $<85°C$ at pressures of 2.67 $\pm$0.07 kPa(a) (20.0 $\pm$0.5 mm Hg). If any naphtha has been collected the receiver should be rotated to present a new one when the vapour temperature reaches 85°C.

23. Continue to collect the LGO distillate until the vapour temperature corresponds to 343°C AET at the pressure registered. Consult the table below which gives combinations of pressure and vapour temperature that yield an AET of 343°C when a K factor of 11.1 is used.

Pressure		Vapour Temperature
kPa(a)	mm Hg	°C
2.60 to 2.64	19.5 to 19.8	209
2.65 to 2.73	19.9 to 20.5	210

Heavy Gas Oil Fraction

24. Present a new receiver and continue the distillation at 2.67 $\pm$0.07 kPa(a) (20.0 $\pm$ 0.5 mm Hg). If necessary, turn up the variable transformer for the bottom heating mantle until the vapour temperature is 270-280°C for liquid hydrocarbon samples or 230-250°C (or 300-340°C pot temperature) for bitumen samples. As necessary, turn on and adjust the temperature of the top heating mantle but ensure that its temperature is less than the vapour temperature. At the specified temperature turn off the reflux timer, spinning band and magnetic stirrer in the sequence specified and immediately lower the heating mantle. The variable transformer for the heating mantle is not turned off.

i) Close stopcock D to all lines and screw plunger E tightly closed (see Figure 3).

ii) Close stopcock J and cautiously open stopcock I to the atmosphere.

iii) Remove LGO receiver(s), stopper and replace with new one(s). Do not remove the HGO receiver.

iv) Return stopcock I to its original position (closed to atmosphere, open to system) and slowly open stopcock J to evacuate the system using the secondary vacuum pump. After 1 to 2 minutes, close stopcock J and turn stopcock D very slowly to its original position. Open screw plunger E.

Weigh the stoppered LGO receiver(s) to the nearest 0.001 g.

25. Distillation of the remainder of the HGO fraction in the sample is conducted at approximately 80 kPa(a) (0.6 mm Hg) pressure. Cool until the pot temperature and vapour temperature are less than 150°C before applying this vacuum. Adjust needle valve A (Figure 1) on the bleed line until the McLeod gauge indicates a pressure of 80 ± 7 Pa(a) (0.60 ± 0.05 mm Hg). Note that the mercury level in the McLeod gauge is initially adjusted to the second zero mark with pressure readings taken from the center scale (see Figure 4). Pressures below 67 Pa(a) (0.5 mm Hg) cannot be used because of the pressure drop between the still head and McLeod gauge. (a)

26. Raise the heating mantle to surround the lower half of the still pot. Switch on the magnetic stirrer. Turn on and adjust the variable transformer controlling the heating tape on the column delivery arm to provide a temperature of approximately 100°C. Turn down the variable transformer for the bottom heating mantle to 70 V when the vapour temperature begins to rise. Activate the spinning band when sufficiently lubricated and turn on the reflux timer when a condensation rate of 2 drops/second has been established. Use the table below as a guide for switching on the reflux timer.

If the HGO part of the distillation is rushed a smooth distillation curve will not be obtained.

Vapour Temperature at 2.67 kPa(a) (20.0 mm Hg) Pressure °C	AET °C	Vapour Temperature at 80 kPa(a) (0.60 mm Hg) Pressure °C
Liquid Hydrocarbons		
270	412	189
271	413	190
272	414	191
273	415	191
274	416	192
275	417	193
276	419	195
277	420	195
278	421	196
279	422	197
280	423	198
Bitumen		
230	366	153
231	367	154
232	368	154
233	370	156
234	371	157
235	372	157
236	373	158
237	374	159
238	375	160
239	376	161

Vapour Temperature at 2.67 kPa(a) (20.0 mm Hg) Pressure °C	AET °C	Vapour Temperature at 80 kPa(a) (0.60 mm Hg) Pressure °C
240	378	162
241	379	163
242	380	164
243	381	164
244	382	165
245	383	166
246	384	167
247	386	168
248	387	169
249	388	170
250	389	171

Monitor the temperature within the still pot very closely. Normally the pot temperature rises at a rate of 3 ± 1°C/mL of condensate collected. After a few mL of distillate have been collected both the rate of temperature rise and the condensation rate will subside. At this point advance the variable transformer setting for the bottom heating mantle to 75 V (and later to 80 V, if necessary) to maintain the required temperature control. Record the vapour temperature and pot temperature at every mL of condensate collected. Monitor and record system pressure several times during the distillation of the HGO fraction.

27. Continue the distillation until the observed vapour temperature corresponds to 524°C AET at the pressure registered. Consult the table below which gives various combinations of pressure and vapour temperature that yield an AET of 524°C when a K factor of 11.1 is used.

Pressure		Vapour Temperature
Pa(a)	mm Hg	°C
73 to 76	0.55 to 0.57	279
77 to 80	0.58 to 0.60	280
81 to 83	0.61 to 0.62	281
84 to 87	0.63 to 0.65	282

Record the still pot temperature when the 524°C AET is reached. For samples containing little residue, it may not be possible to reach a 524°C AET end point. Discontinue the distillation when there is insufficient material in the still pot to allow the distillation to proceed. If the pot temperature reaches 360°C for bitumen samples, record the vapour temperature at that point and discontinue the distillation. Switch off the reflux timer, power to the bottom heating mantle, spinning band, and magnetic stirrer in that order and immediately lower the heating mantle. Allow the fraction cutter to drain and then position a new receiver. Remove, stopper, and weigh the HGO receiver(s).

28. For bitumen samples begin to flow nitrogen in the nitrogen tubing. Connect it to the "T" on the surge tank. Switch off the vacuum pumps one at a time. Slowly open the bleed on the surge tank while observing the mineral oil trap. If the mineral oil begins to rise out of the trap the bleed is being opened too quickly and should be adjusted. When the system is at room pressure disconnect the nitrogen tubing from the T and turn off the nitrogen. Remove the still pot from the column. Stopper lightly and weigh to the nearest 0.01 g when cooled.

    For liquid hydrocarbon samples, remove the still pot.

Hold-up and Column Cleaning

29. Fill a 50 mL still pot approximately 2/3 full with toluene. Add a small magnetic stirring bar and attach the flask to the distillation column. Ensuring tht stopcock D is open to the atmosphere, raise the heating mantle, set the variable transformer to 60 V, and begin heating. Toluene condensate descending down the column will dissolve residual hydrocarbons contained in the system and carry them down to the flask.

30. After the toluene vapours climb at least 1/3 up the condenser, turn on the spinning band and reflux timer. Collect the distillate in a clean receiver. When the column is clean, switch off all equipment and lower the heating mantle. Transfer the contents of the flask and receiver to a previously weighed (0.001 g) crucible. Allow the toluene to evaporate overnight at ambient temperatures and weigh crucible to obtain the amount of hold-up.

Cleaning the Still Pot

31. For bitumen samples add liquid nitrogen to the residue in the still pot. When the mass is sufficiently brittle, break into small pieces with a spatula. Empty the broken material into a clean sample container if further analytical use is required. The wall of the flask can be cleaned by immediately rinsing with toluene.

Calculations: **A. Distillation Curve**

In order to construct a distillation curve from distillate volumes and corresponding vapour temperatures, it is necessary to convert vapour temperatures to atmospheric equivalent temperatures and volumes to volume percents. The former is accomplished using the Sydney Young equation (2) for the atmospheric distillation and the Maxwell and Bonnell equation (3,4) for distillation under reduced pressures. The Maxwell and Bonnell equations presented below have been modified to accommodate degrees Celcius inputs and corrected for the effect of hydrocarbon type (UOP Characterization Factor K).

1. Sydney Young Equation

$$AET\ (°C) = T_v + 0.00012\ (760\text{-}P)\ (273 + T_v)$$

where: T_v = vapour temperature (°C)

$$P = \frac{\text{pressure (Pa(a))}}{133.3} = \text{pressure (mm Hg)}$$

2. Maxwell and Bonnell Equation

$$AET\ (°C) = \frac{5}{9}\left(\left[\frac{748.1A}{\frac{1}{1.8T_v + 491.6} + 0.2145A - 0.0002867}\right] - 491.6\right) + \Delta T$$

where: A = constant related to the vapour pressure derived from data in reference 4

$$= \frac{7.6723 - \log P}{3410.77}$$

ΔT = correction for the K-factor

$$= 5/9 \log\left(\frac{760}{P}\ [\ -2.5\ (K - 12.0)\ ]\right)$$

T_v = vapour temperature (°C)

$$P = \frac{\text{pressure (Pa(a))}}{133.3} = \text{pressure (mm Hg)}$$

3. Volume % Distillate

$$\text{Volume \% Distillate} = \frac{\text{Cumulative Volume of Distillate (mL)}}{\text{Sample Weight (g)}} \times \text{Sample Density (kg/L)} \times 100$$

Report temperature to the nearest whole number and volume % distillates to the nearest 0.1%. Plot volume % distillate versus AET (°C) on rectangular coordinate paper to provide a distillation curve characteristics of the original sample.

B. Distillate Yields

1. Naphtha Fraction (IBP – 195°C AET)

$$\text{Weight \%} = \frac{\text{Weight Naphtha Fraction}}{\text{Sample Weight}} \times 100 \quad (1)$$

If a significant volume of residual water distilled over with the naphtha fraction (>0.1 mL), correct sample weights and weight of naphtha collected by subtracting from these the observed volume of water (1 mL H_2O = 1 g).

2. Light Gas Oil Fraction (195 – 343°C AET)

$$\text{Weight \%} = \frac{\text{Weight LGO Fraction}}{\text{Sample Weight}} \times 100 \quad (2)$$

3. Heavy Gas Oil Fraction (343 – 524°C AET)

$$\text{Weight \%} = \frac{\text{Weight HGO Fraction}}{\text{Sample Weight}} \times 100 \quad (3)$$

4. Residue (>524°C AET)

$$\text{Weight \%} = \frac{\text{Weight Residue}}{\text{Sample Weight}} \times 100 \quad (4)$$

5. Hold-up

$$\text{Weight \%} = \frac{\text{Weight Hold-up}}{\text{Sample Weight}} \times 100 \quad (5)$$

6. Total Recovery

Weight % = (1) + (2) + (3) + (4) + (5)

Precision: Precision data reflecting the repeatability of weight % distillate fraction determinations for a typical bitumen and virgin gas oil are indicated below. Results are based on 4 or more complete distillations performed by a single operator on charges obtained from homogenous stock.

	Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
Bitumen			
LGO	12.50	±0.16	1.25%
HGO	27.24	±0.53	1.96%
Residue	58.23	±0.29	0.50%
Recovery	99.26	±0.10	0.10%
Virgin Gas Oil			
Naphtha	2.18	±0.12	5.32%
LGO	22.84	±0.44	1.91%
HGO	67.17	±0.27	0.40%
Residue	5.59	±0.10	1.74%
Recovery	99.58	±0.13	0.13%

For the bitumen sample the distillations were discontinued when cracking became evident.

Comments:

a. A 67 Pa(a) (0.5 mm Hg) lower limit to the pressure is characteristic of the particular arrangement employed by Syncrude Research.

References:

1. Yost R.W., "Distillation Primer, Survey of Distillation Systems" American Laboratory, January, 1974, p 63.

2. ASTM. "Distillation of Petroleum Products" Annual Standards (1976), Part 23, Method D 86.

3. Maxwell J.B. and Bonnell L.S., "Derivation and Precision of a New Vapour Pressure Correlation for Petroleum Hydrocarbons", Ind. Eng. Chem., 49, 1187 (1957).

4. Maxwell J.B. and Bonnell L.S., "Vapor Pressure Charts for Petroleum Hydrocarbon", Esso Research and Engineering Co., Linden, NJ, April 1955. Available on request.

5. UOP. "Calculation of UOP Characterization Factor and Estimation of Molecular Weight of Petroleum Oils." UOP Laboratory Test Methods for Petroleum and its Products, Universal Oil Products Co., Des Plaines, IL.

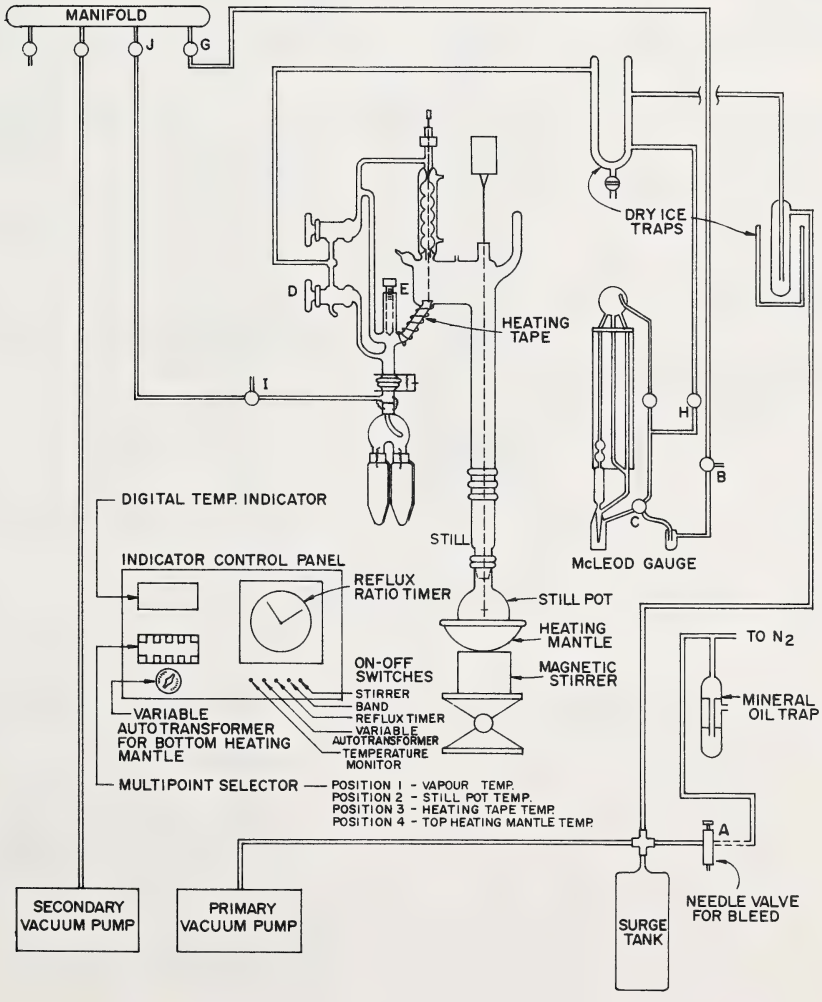


FIGURE 1: COMPLETE DISTILLATION ASSEMBLY

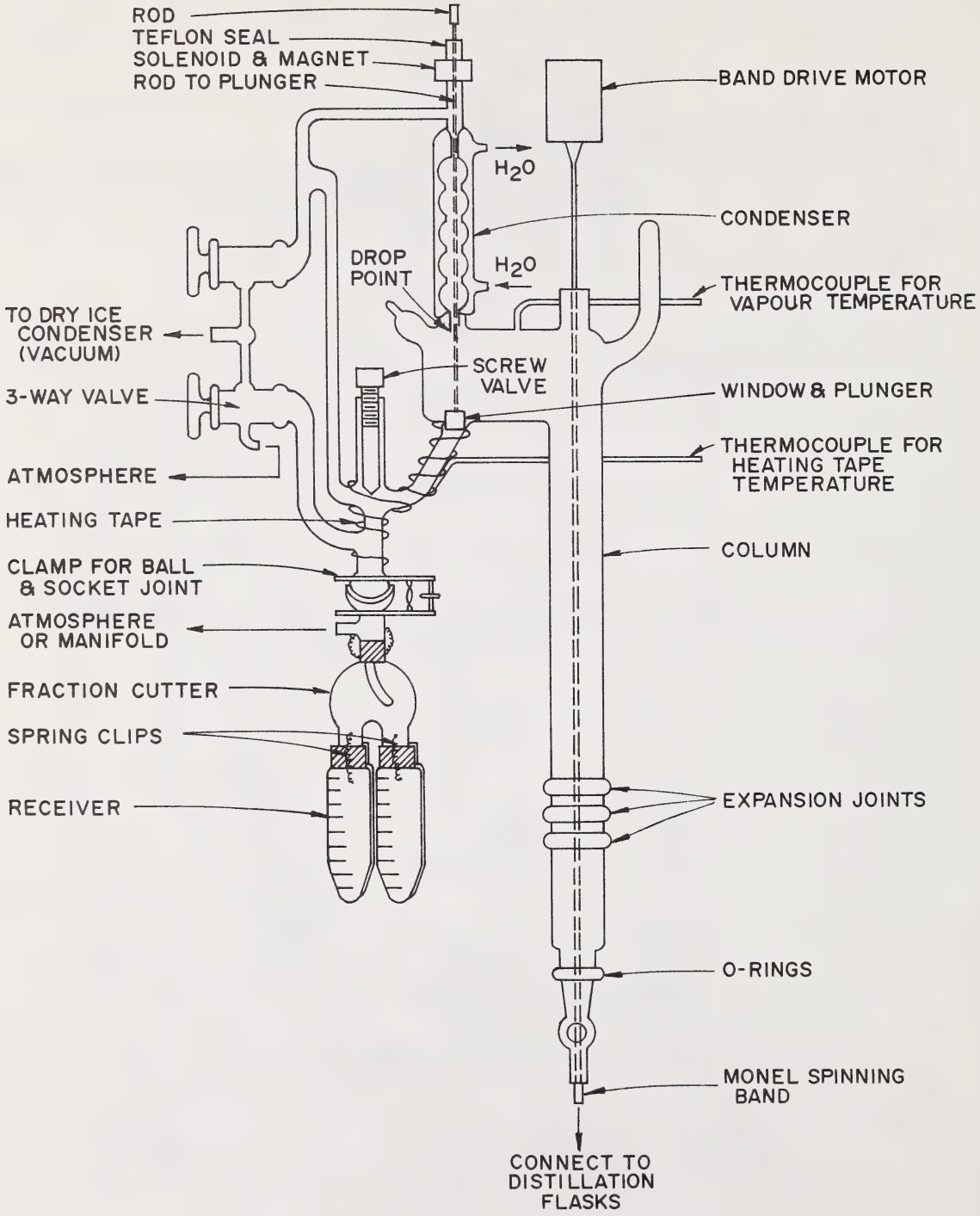


FIGURE 2: DISTILLATION APPARATUS

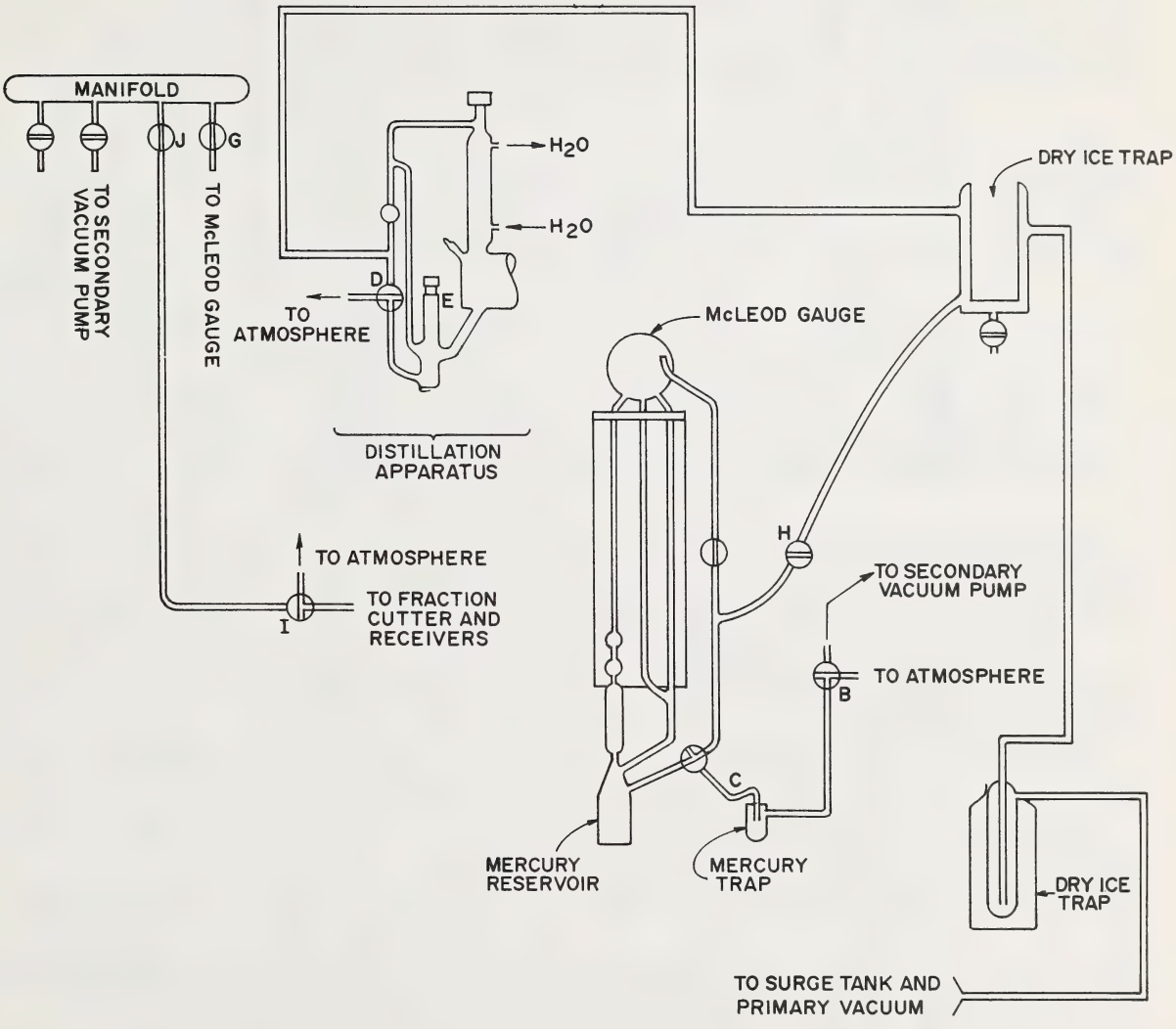


FIGURE 3: SYSTEM LAYOUT FOR VACUUM DISTILLATION

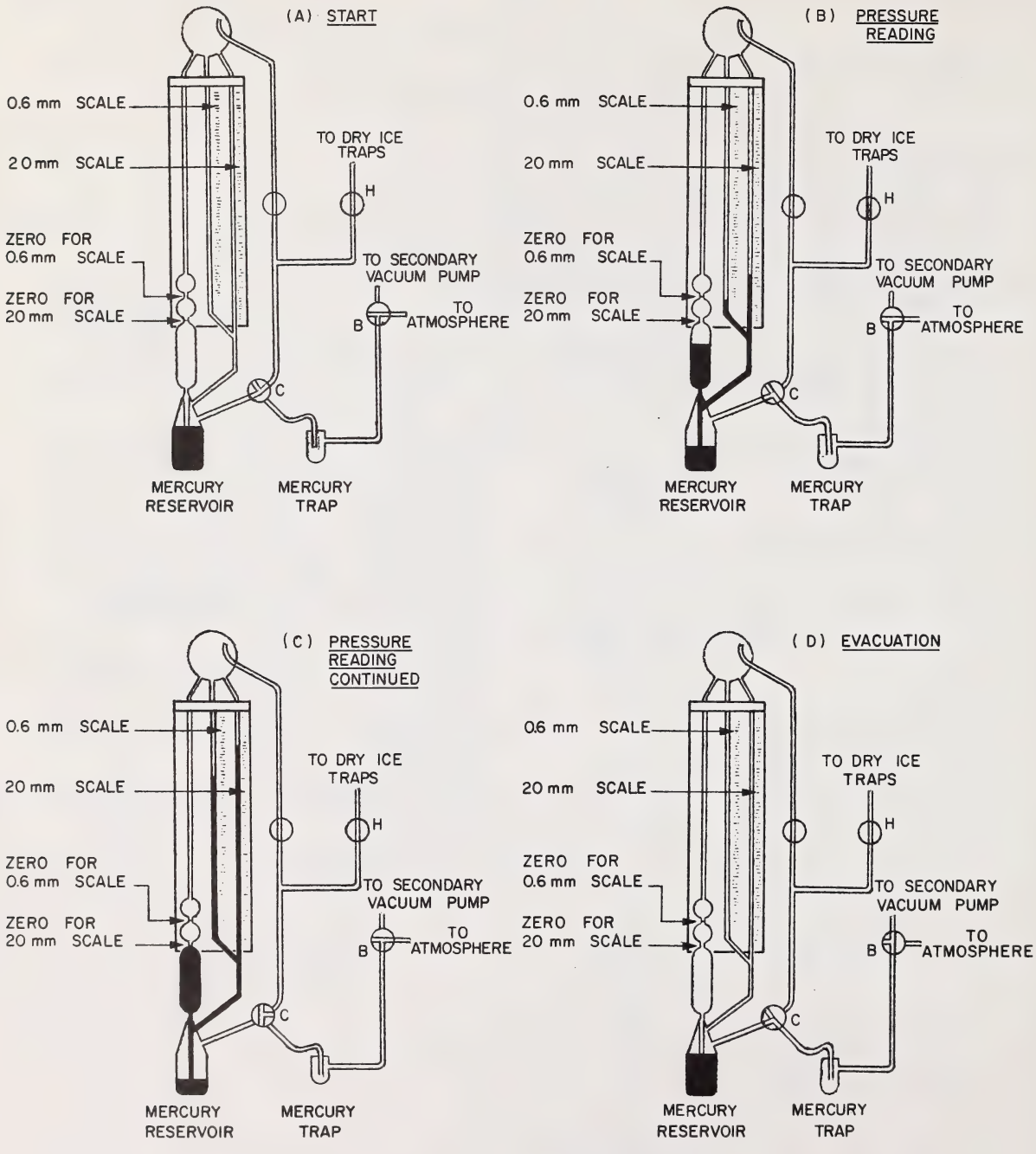


FIGURE 4: McLEOD GAUGE OPERATION

Gas Chromatographic Simulated Distillation of Hydrocarbon Samples Containing Non-Volatile Residue

Scope: This procedure is an adaptation of the ASTM "Proposed Test Method for Boiling Range Distribution of Crude Petroleum by Gas Chromatography" (1). It is primarily intended for the simulated distillation of bitumen and samples that contain large amounts of non-volatile residue. The procedure may also be applied to heavy gas oil samples that have a final boiling point in excess of 525°C.

Summary: Two chromatographic analyses are performed to characterize the sample. The volatile components of the sample are analyzed by a standard simulated distillation procedure. A separate assay is done to determine the amount of volatile material in the sample by an internal standard technique. The data from the simulated distillation is then corrected for the non-volatile residue, and results are reported as percentages of the total sample.

Background: The simulated distillation of volatile petroleum hydrocarbons has traditionally been performed by ASTM D 2887 (2). Bitumen, however, contains a considerable amount of material that is not volatile and cannot be directly determined by gas chromatography. Some heavy gas oil fractions may also contain a small amount of material with atmospheric equivalent boiling temperatures exceeding 525°C. In order to accurately describe such samples by simulated distillation special provision must be made to account for this high boiling or residue material. The method described herein supplements simulated distillation data by also determining the fraction of sample which is volatile.

The procedure differs from the proposed ASTM method (1) in two ways. First, a single compound (naphthalene) is used as the internal standard rather than the four paraffins specified by the ASTM procedure. A second difference is the incorporation of a response factor calibration in the procedure, which serves to improve the accuracy of the residue determination.

A recommended resource is the ASTM publication "Calculation of Physical Properties of Petroleum Products From Gas Chromatographic Analyses" (3).

Interferences:

1. The chromatographic data may be adversely affected by improper operating conditions, especially septum and column bleed.
2. The determination of non-volatile residue is instrument and operator sensitive. The most sensitive aspects of the analysis are obtaining a material for response factor calibration that represents the material in the sample and maintaining identical conditions, especially sample size, for the calibration and assay of the sample.

Safety Considerations:

1. Hydrogen — extremely flammable. High explosion hazard.
2. Carbon disulfide — highly toxic by inhalation and skin absorption. Extremely flammable. High explosion hazard.
3. Naphthalene — moderately toxic by inhalation and skin absorption.

Apparatus, Reagents, Materials:

1. Gas chromatograph — Varian model 2860-30 with the following features:
   i) sub-ambient (liquid CO_2) and temperature programming capabilities;
   ii) dual flame ionization detectors;
   iii) heated flash vapourization injection ports with glass liners;
   iv) flow controllers.

   Varian Associates Inc., 611 Hansen Way, CA 94303.
2. Columns — matched 450 mm x 2 mm ID stainless steel packed with 10% SE-30 on Chromosorb P AW, 80/100 mesh.

3. Integrator — Spectra-Physics Minigrator, Spectra-Physics,2905 Stender Way, Santa Clara, CA 95051.
4. Strip chart recorder — single pen, 1 mV full scale.
5. Analytical balance.
6. Syringes — 1.0 and 0.1 μL.
7. Syringe cleaner — Hamilton 15370.
8. Septa — Supelco Thermogreen LB-1. Supelco Inc. Supelco Park, Bellefonte, PA 16823.
9. Molecular sieve traps — type 5A.
10. Helium — 99.995%, oxygen and moisture free.
11. Air — hydrocarbon free.
12. Hydrogen — hydrocarbon free.
13. Calibration mixture — blend of equal weights of normal paraffins C_5 to C_{44} dissolved in carbon disulfide.

Procedure: Preparation of Apparatus

1. Ensure that the carrier gas is oxygen free. If necessary, a suitable gas purifying apparatus should be installed. Activated 5A molecular sieve traps are placed between the flow controllers and the injection ports.
2. Commission the chromatograph and set the detector temperature to 400°C. Set the injector temperature to 280°C, and allow the septa to condition overnight in the injection port before assaying samples.
3. Condition the columns overnight at 350°C with a helium flow of 0.50 mL/s. Carefully check for leaks before conditioning the columns. Do not connect the columns to the detector during conditioning, but terminate the column outlets with a short length (approximately 150 mm) of capillary tubing to prevent diffusion of air into the column outlets.
4. Cool the oven and connect the columns to the detectors when conditioning is complete. Establish the detector air and hydrogen flows. Ignite and balance the detectors following the instrument manual instructions. Set the electrometer to present a differential (A-B) mode of operation, and set the electrometer sensitivity to 10^{-9} A full scale.
5. Set the integrator peak width parameter to five seconds, and the slope sensitivity parameter to a value of 10. Set the integrator operating mode to normal, i.e. to report discrete peaks.
6. Cool the oven to −40°C and allow it to equilibrate for four minutes. Inject a volume of the C_5 to C_{44} normal paraffin calibration mixture, such that the peaks are 50 to 90% of full scale at a sensitivity of 10^{-9} A with an attentuation factor of x 4. Start the integrator and initiate a temperature program at 0.13°C/s to a final temperature of 350°C.
7. While the oven is at 350°C adjust the carrier gas flow rate through the reference column, if necessary, to minimize any shift of the baseline from that established at −40°C.
8. Identify the peaks on the chromatogram and record the retention times. Perform a linear regression of the boiling temperatures in °C versus the retention times for all data points from C_5 to C_{44}. This constitutes a calibration and may be used as such later if the operating parameters, especially carrier flow rate, have not changed. At this point, use the linear regression as a diagnostic test of the system's performance. The coefficient of determination, r^2, must be at least $r^2 = 0.999$. Failure of this test may imply pneumatic or thermal problems which must be remedied. In addition to calibration linearity, good baseline stability is required.

Calibration of Retention Times

9. The retention time calibration should be performed after any change in carrier gas flow rate and at least once per week. Set the integrator to the discrete peak mode. Inject a sample of the C_5 to C_{44} normal paraffin calibration standard and temperature program from $-40°C$ to 350°C at 0.13°C/s. Identify the peaks, record the retention times and perform a linear regression of the boiling temperatures in °C versus the rention times. The coefficient of determination, r^2, including all data points from C_5 to C_{44} should be 0.999. Record the slope and the intercept of the linear regression.

Calibration of Response Factors

10. Obtain a heavy gas oil standard of similar origin to the sample to be analyzed using Method 5.2.

11. Gravimetrically prepare a calibration standard containing 1% naphthalene and 99% of the heavy gas oil prepared in Step 10. Record the weights and calculate the weight ratio of weight heavy gas oil/weight naphthalene. Add an equal volume of carbon disulfide and mix.

12. Set the integrator to the simulated distillation mode to report the accumulated area every five seconds. Set the chromatograph oven to $-40°C$, inject 1 μL of the heavy gas oil/naphthalene calibration standard, start the integrator and initiate a temperature program of 0.13°C/s to 350°C. Inhibit integration manually until the recorder indicates the baseline disturbance due to the solvent has passed.

13. From the strip chart recording, determine the time when the naphthalene is completely eluted. Determine from the integrator output the peak area due to the naphthalene.

14. From the boiling temperature versus retention time calibration, calculate the retention time corresponding to a boiling temperature of 525°C. Inspect the chromatogram and observe whether the heavy gas oil has returned to baseline at this time.

    If the baseline has been achieved by the 525°C retention time, record the area due to the heavy gas oil. Calculate the area ratio of area heavy gas oil/area naphthalene.

    If the heavy gas oil used in preparing the standard contains material that has a boiling point greater than 525°C, record the area boiling below 525°C and the total area of the heavy gas oil. Assume complete recovery of the heavy gas oil and calculate the portion of the heavy gas oil with boiling temperature less than 525°C. Correct the sample weight in step 11, and recalculate the weight ratio:

$$\text{Weight Ratio} = \frac{\text{Weight Heavy Gas Oil bp} < 525°C}{\text{Weight Naphthalene}}$$

    Calculate the area ratio:

$$\text{Area Ratio} = \frac{\text{Area Heavy Gas Oil bp} < 525°C}{\text{Area Naphthalene}}$$

15. Calculate the relative response factor RRF:

$$\text{RRF} = \frac{\text{Weight Ratio}}{\text{Area Ratio}}$$

    This factor should be constant, but in practice it may be dependent upon the amount of sample injected. It is also sensitive to baseline drift. Therefore, ensure that the baseline sensed by the integrator does not drift and that the sample peak generated below has a similar size as the standard.

Analysis of Samples

16. Two chromatographic runs are required to characterize the samples. The first run is a standard simulated distillation. It also permits an estimate of the amount of sample that should be injected to give a peak of the proper size for the second run with the internal standard. Prepare a portion of the sample for a standard simulated distillation by adding carbon disulfide, as required, to reduce the viscosity.

17. Set the integrator to a simulated distillation mode that reports the accumulated area every five seconds. Cool the column oven to −40°C, inject a volume equivalent to 1 μL of neat sample, start the integrator, and initiate a temperature program at 0.13°C/s to 350°C. Retain the chromatogram and integrator printout for calculations.

18. Prepare a portion of the sample for the internal standard assay, by gravimetrically adding approximately 2 wt % naphthalene to the sample. Add a volume of CS_2 equal to the sample volume and mix. From the peak size obtained in the preceeding step, estimate the sample volume required to generate a peak of the same size as that obtained in the response factor calibration. Set the column oven to −40°C, inject the required volume, start the integrator and temperature program. Retain the chromatogram and integrator printout for calculations.

Calculations: The calculations are performed in two steps. The first step determines the fraction of the sample that is volatile i.e. boiling point < 525°C. The second step calculates the distillation curve of this material.

Percentage Volatiles in Sample

The area of the internal standard and the area of the sample are required to calculate the percent volatiles in the sample. This information may be directly accessible if the initial boiling point of the sample is sufficiently high that no sample elutes with the naphthalene. If part of the sample and naphthalene elute together, a more involved calculation is required to allow for the overlap.

Non-overlap Case

1. From the area of the sample with boiling point less than 525°C and the area of the naphthalene calculate the area ratio.

$$\text{Area Ratio} = \frac{\text{Area for Sample bp} < 525°C}{\text{Area for Naphthalene}}$$

2. The % volatile is given by:

$$\%\ \text{Volatiles} = \text{Area Ratio} \times \text{RRF} \times \frac{\text{Wt. Naphthalene}}{\text{Wt. Sample}} \times 100$$

Overlap Case

3. The chromatogram is considered in three segments — material eluting before, with, and after the naphthalene. From the chromatogram without internal standard the material eluting in the region where naphthalene elutes may be determined relative to the areas in the overlap-free regions. Data from the chromatogram with internal standard is then assigned to similar segments, and the areas due to the sample and due to the naphthalene in the naphthalene window are calculated. The percent volatiles in the sample is then calculated as in the case without overlap.

4. From the calibration run to determine the relative response factor, determine the times when the naphthalene rises from and returns to the baseline. This time interval is designated as the naphthalene window.

5. Examine the integrator data from the simulated distillation without internal standard and read:

   A = area due to material eluting before the naphthalene window

   B = area due to material eluting within the naphthalene window

   C = area due to material eluting after the naphthalene window but before the time corresponding to 525°C

   Express the amount of sample material within the naphthalene window, D, as a ratio of the sum of the other two areas:

$$D = \frac{B}{A + C}$$

6. Examine the integrator data from the simulated distillation with internal standard and read:

   E = area due to material eluting before the naphthalene window

   F = area due to material eluting within the naphthalene window

   G = area due to material eluting after the naphthalene window but before the time corresponding to 525°C.

   Calculate the area, H, due to the sample that falls within the naphthalene window of the simulated distillation with the internal standard:

   $H = (E + G)\ D$

7. Calculate the total area due to the sample for the simulated distillation with internal standard.

   Area for Sample = E + G + H

8. Calculate the area due to the naphthalene for the simulated distillation.

   Area for Naphthalene = F − H

9. Calculate the area ratio:

$$\text{Area Ratio} = \frac{\text{Area for Sample}}{\text{Area for Naphthalene}}$$

10. The % volatiles is given by:

$$\%\ \text{Volatiles} = \text{Area Ratio} \times \text{RRF} \times \frac{\text{Wt. Naphthalene}}{\text{Wt. Sample}} \times 100$$

Simulated Distillation Calculation

The simulated distillation for sample material boiling below 525°C is calculated from the data generated in the run without internal standard. The area due to all material eluting to the 525°C cut point is defined as equal to the % volatiles, determined in the above calculations. The distillation curve is constructed by calculating from retention times the temperatures corresponding to 0.5,1,2,3,4,5,10,15 . . . percent of the area that would have been observed if the entire sample had been eluted.

11. From the integrator printout for the simulated distillation of the sample without internal standard, determine the total area up to the retention time corresponding to a boiling point of 525°C.

12. Calculate the total area, X, that would have been observed if the entire sample had been eluted.

$$X = \frac{\text{Area to 525°C}}{\%\ \text{Volatiles}} \times 100$$

13. For each point on the distillation curve, the boiling temperature is calculated as follows:

    i) Calculate the area, Y, corresponding to the desired % off.

    $$Y = \frac{(\%\ \text{off})\ X}{100}$$

    ii) From the integrator printout, find the two area-time data points that bracket the area, Y, corresponding to the desired % off. The lower area and time are designated A_1 and T_1. The higher area and time are designated A_2 and T_2.

    iii) Perform a linear interpolation to determine the retention time, T_{off}, corresponding to the desired % off.

    $$T_{off} = \frac{(Y - A_1)\ (T_2 - T_1)}{(A_2 - A_1)} + T_1$$

    iv) Calculate the boiling point, BP, corresponding to the time at the desired % off from the boiling point-retention time calibration data:

    $$BP = \text{Slope}\ (T_{off}) + \text{Intercept}$$

    Generate boiling point data to correspond to 0.5,1,2,3,4,5,10,15 . . .% off.

14. Tabulate data, and if required, plot the distillation curve with boiling point as ordinate and % off as abscissa. Report material with boiling point greater than 525°C as residue.

Precision: To be determined.

References:

1. ASTM Committee D-2. "Proposed Test Method for Boiling Range Distribution by Gas Chromatography." Annual Standards (1976), Part 25, pp 716-722.
2. ASTM. "Boiling Range Distribution of Petroleum Fractions by Gas Chromatography." Annual Standards (1976), Part 24, Method D 2887.
3. ASTM Committee D2. "Calculation of Physical Properties of Petroleum Products from Gas Chromatographic Analyses." ASTM Special Technical Publication 577 (1973).

Determination of Conradson Carbon Residue of Bitumen and Distillation Residues

Scope: This method determines the amount of carbon residue left after evaporation and pyrolysis of bitumen or distillation residues, and is intended to provide some indication of relative coke-forming properties. The amount of Conradson Carbon Residue is also corrected for the presence of mineral matter in the sample.

Summary: A weighed quantity of sample is placed in a crucible and subjected to destructive distillation. The residue undergoes a cracking and coking reaction during severe heating for a fixed period of time. The crucible containing the carbonaceous residue is cooled in a desiccator and weighed. This residue is subsequently reduced to an ash by heating in a muffle furnace at 750°C, allowed to cool, and weighed. The amount of residue is corrected for the ash content and reported as Conradson Carbon Residue (C.C.R.).

Background: The term "carbon residue" is used here to denote the carbonaceous residue formed after evaporation and pyrolysis of a petroleum product. The residue is not entirely composed of carbon, but is a coke which can be further changed by heating.

The method was originally devised to determine the carbon forming tendencies of diesel fuels and lubricating oils in internal combustion engines (1). Carbon residue values of bitumen and of distillate residue samples are indicative of the coke yields to be expected from these materials in refinery coking operations.

The application of the ASTM Conradson Carbon Residue determination to bitumen has resulted in two innovations. Bitumen samples generally contain an appreciable amount of mineral matter. The amount is variable and depends upon the method of preparation. Accordingly, a correction for suspended solid matter is made by carrying out an ash determination on the carbon residue. Secondly, due to the high Conradson Carbon Residue contents of bitumen samples, a smaller sample size is used together with correspondingly shorter burning and flame times.

It should be noted that carbon residue values determined by this method are not the same as those obtained using the Ramsbottom procedure (2), nor have satisfactory correlations between the two methods been established for bitumen samples.

Safety Considerations: Open flames are used in this method. Ensure no flammable solvents or other combustible materials are close by.

Apparatus, Reagents, Materials:

1. Coors crucible — 30 mL, low wide form, glazed inside and out.
2. Skidmore iron crucible, flanged, with cover.
3. Spun sheet-iron crucible, with cover.
4. Wire support — bare 2.3 mm diameter Nichrome wire.
5. Hollow sheet-metal insulator — 150 to 175 mm diameter.
6. Sheet-iron hood.
7. Support stand.
8. Meker-type burner.
9. Clean, dry sand.
10. Glass beads — 3 mm diameter.
11. Muffle furnace.
12. Analytical balance.

A more complete description of the apparatus may be found in Reference 1.

Procedure:

1. Heat a 30 mL crucible containing two glass beads in a muffle furnace at 750°C for 30 minutes. Allow to cool in a desiccator and weigh to the nearest 0.1 mg.
2. Weigh, to the nearest 0.1 mg, a 2 g sample of bitumen or distillation residue into the tared 30 mL crucible containing the two glass beads (a, b). Place this crucible in the center of the Skidmore crucible. Level approximately 25 mL of sand in the large sheet-iron crucible and set the Skidmore crucible on it in the exact center of the iron crucible. Apply covers to both the Skidmore and the iron crucible. The cover on the latter fits loosely to allow free exit to the vapors as formed.
3. Place the bare Nichrome wire triangle on the stand and then the sheet-metal insulator upon the triangle. Center the sheet-iron crucible in the insulator with its bottom resting on top of the triangle, and cover with the hood in order to distribute the heat uniformly during the process.
4. Apply heat with a high, strong flame from the Meker-type burner, so that the pre-ignition period will be 6 ± 1.5 minutes. The exact setting on the burner will have to be determined by trial and error. If too short a pre-ignition time is used, the distillation may start too rapidly and cause foaming or too high a flame. When smoke appears above the chimney, immediately move or tilt the burner so that the gas flame plays on the side of the crucible and ignites the vapors. Then remove the heat temporarily, and before replacing, decrease the gas flow to the burner so that the ignited vapors burn uniformly with the flame above the chimney but not above the wire bridge. Increase the heat, if necessary, when the flame does not show above the chimney. The period of burning the vapors shall be 10 ± 1.5 minutes. If it is impossible to meet the requirements for both the flame and the burning time, the requirement for the burning time is the more important.
5. When the vapors cease to burn and no further blue smoke can be observed, turn on the burner as far as possible to make the bottom and lower part of the sheet-iron crucible a cherry-red. Maintain heating for exactly 5 minutes. The total period of heating shall be 21 ± 3 minutes.
6. Remove the burner and allow the apparatus to cool until no smoke appears (approximately 15 minutes). Then remove the hood and the covers from the crucibles. Remove the 30 mL Coors crucible with tongs, place in a desiccator, cool and weigh.
7. Place the Coors crucible containing the carbon residue into the muffle furnace at 750 ± 25°C until all carbonaceous material has disappeared (about 1 to 4 hours). Cool the crucible in a desiccator and weigh.

Calculations:

1. Calculate the Conradson Carbon Residue of the sample (b) as:

$$\% \text{ C.C.R.} = \frac{B - C}{A - C} \times 100$$

2. Calculate the percent ash in the sample as:

$$\% \text{ Ash} = \frac{C}{A} \times 100$$

where: A = weight of sample, g
B = weight of residue, g
C = weight of ash, g

Precision: Data below indicates typical precision associated with C.C.R. determinations on bitumen wherein an ash correction is imposed. Estimates were obtained from the analysis of 4 samples withdrawn from a homogeneous bitumen supply. Ash content averaged 1.84 wt% of the bitumen.

Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
11.81	±0.21	1.78%

Comments:

a. For some distillation residues, sampling is facilitated by the addition of liquid nitrogen to render the sample brittle. In this case, place the crucible and residue in an oven at 110°C to remove any frost that might have formed. Allow the sample to cool in a desiccator for 20 minutes before determining the sample weight.

b. Samples are normally analyzed in duplicate and the average result is reported.

References:

1. ASTM. "Conradson Carbon Residue of Petroleum Products." Annual Standards (1976), Part 23, Method D 189.

2. ASTM. "Ramsbottom Carbon Residue of Petroleum Products." Annual Standards (1976), Part 23, Method D 524.

Determination of the Specific Gravity of Bitumen by the Pycnometer Method

Scope: This method determines the specific gravity of bitumen at 15.6°C. The method is an implementation of ASTM D 70 and is also applicable to the broader range of samples covered by that procedure.

Summary: The ratio of the weight of a given volume of bitumen to the weight of an equal volume of water is determined at 15.6°C.

Safety Considerations: No unusual safety considerations.

Apparatus, Reagents, Materials:

1. Glass pycnometer — Hubbard or Hubbard-Carmick design conforming to ASTM D 70 specifications.
2. 600 mL beaker.
3. Constant temperature bath maintained at 15.6 ± 0.1°C.
4. Thermometer — conforming to ASTM E 1 specifications for thermometer 63C, −8 to +32°C.
5. Hot plate.
6. Analytical balance.
7. Distilled water.

Procedure:

1. Fill a 600 mL beaker with freshly distilled water and place it in a constant temperature water bath maintained at 15.6 ± 0.1°C.
2. Thoroughly clean and dry the pycnometer and stopper, and weigh to the nearest mg.
3. Fill the pycnometer with distilled water, firmly insert the stopper and completely immerse the pycnometer in the beaker. Allow the pycnometer to equilibrate for a minimum of 30 minutes.
4. With the pycnometer and its contents at 15.6°C, expose the top of the stopper and immediately wipe it dry. The meniscus of the water in the bore should now be flush with the top of the stopper.
5. Remove the pycnometer from the beaker of water and dry the outside with a clean dry cloth. Immediately weigh the pycnometer and water to the nearest mg.
6. Empty and dry the pycnometer. Gently heat a 5 to 20 g sample to a fluid condition in order to facilitate transfer of the sample and eliminate air bubbles. Strong heating with a consequent loss of low boiling materials should be avoided. Transfer the sample into the clean dry pycnometer avoiding the inclusion of air bubbles. Ensure the sample does not touch the sides of the pycnometer above the final level. Cool the pycnometer to room temperature and weigh with stopper.
7. Fill the remaining volume of the pycnometer with freshly boiled distilled water and firmly insert the stopper. Place the pycnometer in the beaker of water. Allow at least 30 minutes for equilibration.
8. With the pycnometer and its contents at 15.6°C, expose the top of the stopper and immediately wipe water from it as before. Remove the pycnometer from the beaker of water and wipe all moisture from the outer surface with a clean dry cloth. Immediately weigh the pycnometer.

Calculations:

1. Calculate the specific gravity of the sample as:

$$\text{Specific Gravity (15.6/15.6°C)} = \frac{C - A}{(B - A) - (D - C)}$$

where: A = weight of the pycnometer, g
B = weight of the pycnometer filled with water, g
C = weight of the pycnometer and bitumen, g
D = weight of the pycnometer, bitumen and water, g

All pycnometer weights include the stopper.

2. Calculate the API gravity of the sample as:

$$\text{API Gravity} = \frac{141.5}{\text{Specific Gravity (15.6/15.6°C)}} - 131.5$$

Precision: ASTM D 70 reports a single-operator standard deviation of 0.0013 for the specific gravity.

Reference:

1. ASTM. "Specific Gravity of Semi-Solid Bituminous Materials" ASTM Annual Book of Standards (1976), Part 19, Method D 70.

Determination of Average Molecular Weight of Bitumen and Bitumen Fractions by Freezing Point Depression

Scope: This method determines the average molecular weight (1) of bitumen, bitumen fractions, and other hydrocarbon mixtures with average molecular weights between 150 and 700 g/mol. The samples must be completely soluble and chemically inert in the benzene solvent employed. Molecular weight values represent a number-average molecular weight for the sample components.

Summary: The freezing points for benzene and for a benzene solution containing a known weight of sample are determined from their cooling curves. From the depression of the freezing point due to the sample, the average molecular weight is calculated by application of Raoult's law.

Background: Many methods exist for molecular weight determinations (2) and several have been documented by UOP (3) and ASTM (1,4). Syncrude Research has applied freezing point depression and vapour pressure lowering methods to bitumen and bitumen fractions. The freezing point depression method has been selected for documentation since it is inexpensive to implement and simple to perform.

The average molecular weight of petroleum hydrocarbon mixtures is used in characterization (5) and correlation studies. Also, molecular weight is employed for heat exchange evaluations of distillation columns and for monitoring hydrocarbon cracking processes.

Safety Considerations: Benzene — highly toxic and a suspected carcinogen. Employ strict precautions to prevent inhalation and skin absorption. Extremely flammable.

Apparatus, Reagents, Materials:

1. Freezing Point Depression Apparatus — as shown in Figure 1 and consisting of:
   - i) Cooling bath — a large jar or double walled metal can of sufficient capacity to contain ample cooling medium.
   - ii) Outer tube — a glass container, approximately 130 mm high and 50 mm OD, to serve as an air jacket. It is closed by a rubber stopper which supports an inner tube in which the sample is placed.
   - iii) Inner tube — a large test tube closed by a cork which supports the thermometer and has an opening to act as a guide for the stirrer.
   - iv) Stirrers — two wire stirrers are required. One stirrer has a ring diameter such that the ring is approximately equidistant from the thermometer and the wall of the inner tube. The other stirrer has a ring large enough to slide between the outer tube and the cooling bath.
   - v) Differential thermometer — to read directly to 0.01°C and permit estimates to 0.001°C, −30°C to + 50°C model.
   - vi) Magnifying lens — to distinguish 0.001°C on the differential thermometer.
2. Stop watch.
3. A supply of water and crushed ice (a).
4. Analytical balance.
5. Benzene — A.C.S. reagent grade (b).

Procedure:

1. Fill the cooling container with ice and water allowing for insertion of the outer tube. Introduce approximately 25 g of benzene, weighed to the nearest 0.01 g, to the inner tube. Stopper the tube and partially immerse it in a beaker of crushed ice until solidification begins. Remove the tube from the crushed ice and insert the differential thermometer (c). Stir the partially frozen benzene until the solid disappears. Quickly place the inner tube in the outer tube and transfer to the

cooling container. Initially read the temperature to the nearest 0.001C° at one minute intervals while maintaining uniform stirring. Near the freezing point the measurement interval is reduced to 30 or 15 seconds. Continue temperature readings for about 5 minutes after freezing has occurred. Remove the assembly from the cooling container and place the thermometer in crushed ice.

2. Add approximately 0.5 g of sample, weighed to the nearest 0.1 mg, to the benzene in the inner tube and determine the cooling curve of the solution in the same manner as for benzene.

Calculations:

1. Plot temperature in °C versus time in minutes on rectangular coordinate paper for benzene and for the sample/benzene mixture as shown in Figure 2. The minimum of each cooling curve is attributed to supercooling. The linear portion of the cooling curve after the supercooling region is extrapolated to intersect the linear portion of the cooling curve before the supercooling region. The temperature at the point of intersection is taken as the freezing point.
2. Calculate the average molecular weight of the sample as:

$$M = \frac{W\,(K_f - \Delta T)}{(\Delta T)\,(S)}$$

where: M = number-average molecular weight, g/mol
W = weight of sample, g
K_f = cryoscopic constant for benzene, 65.6
S = moles of solvent
ΔT = freezing point depression, °C
= freezing point of benzene − freezing point of solution

Precision: ASTM D 2224 suggests that results from duplicate determinations should not differ by more than 5% of the higher value.

Comments:

a. Ice and water are normally sufficient to provide a cooling bath at the desired 5 °C below the freezing point of benzene solution. Salt may be added if a lower cooling bath temperature is required.

b. The benzene must be dry. Anhydrous sodium sulfate may be used as a drying agent.

c. The thermometer must be positioned in such a way that the bulb is half way between the bottom of the test tube and the top of the sample. It should also be positioned concentric with the test tube.

References:

1. ASTM. "Mean Molecular Weight of Mineral Insulating Oils by the Cryoscopic Method." Annual Standards (1976), Part 40, Method D 2224.
2. Siggia, S. Survey of Analytical Chemistry. McGraw-Hill Book Co., New York, 1968.
3. UOP. "Molecular Weight of Petroleum Fractions by Cryoscopic Method." UOP Laboratory Test Methods for Petroleum and its Products, 4th Edition, Method 103, Universal Oil Products Co., Des Plaines, IL, 1959.
4. ASTM. "Estimating Apparent Vapour Pressure and Molecular Weights of Lubricating Oils." Annual Standards (1976), Part 24, Method D 2878.
5. ASTM. "Calculation of Carbon Distribution and Structure Group Analysis of Petroleum Oils by the n-d-M Method." Annual Standards (1976), Part 25, Method D 3238.

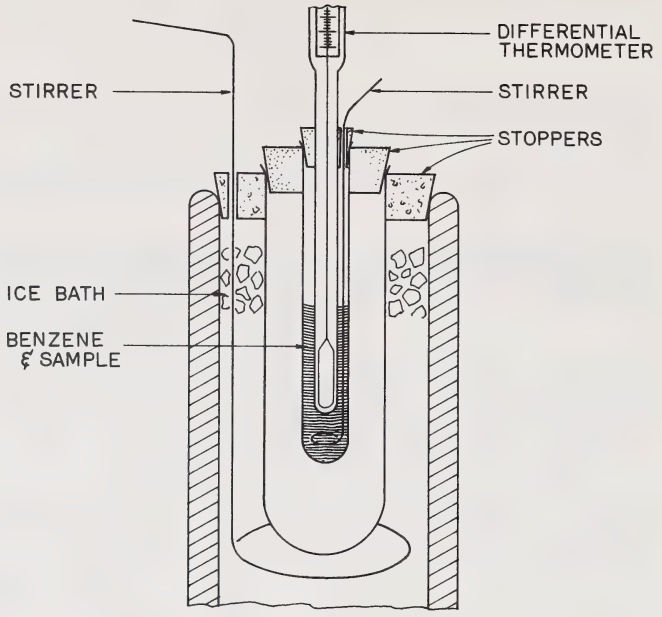


FIGURE 1. FREEZING POINT DEPRESSION APPARATUS

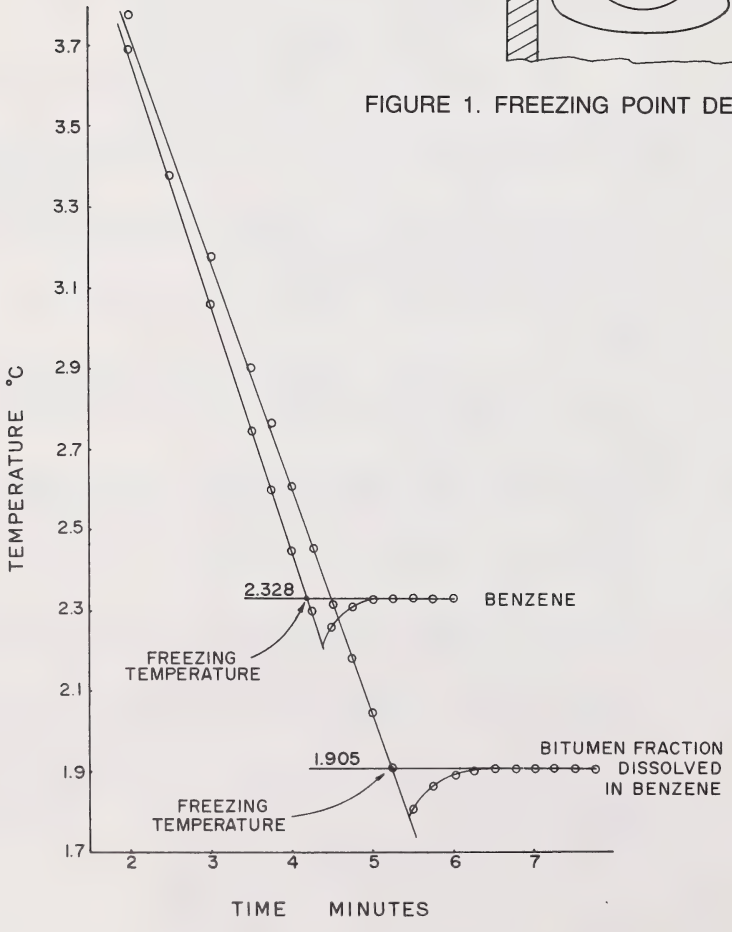


FIGURE 2. COOLING CURVE

Determination of Bromine Number for Liquid Petroleum Hydrocarbons by the Electrometric Method

Scope: This method determines the bromine number of liquid petroleum hydrocarbons. The procedure is a modification of ASTM D 1159 "Bromine Number of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration."

Summary: The sample is initially dissolved in a solvent consisting of glacial acetic acid, 1,1,1-trichloroethane, methanol and sulfuric acid. The solution is titrated with bromide-bromate titrant using dual platinum electrodes and a 10 μA polarizing current for end point detection.

Background: Bromine number is the number of grams of bromine consumed by 100 g of sample when reacted under specified conditions. The two generally accepted standard bromine number methods are the ASTM D 1159 procedure and UOP Method 304. There are a number of differences between the methods which are significant.

The ASTM procedure uses a polarized electrode pair. As soon as there is a small amount of excess bromine the solution conductivity increases sharply, producing a large clearly defined deflection at the end point. The glass-platinum electrode pair recommended in the UOP method produces a potential which is proportional to the bromine concentration. In practice, the latter method produces less clearly defined end points.

The UOP method uses mercuric chloride as a catalyst to speed up the bromination reaction. The ASTM procedure does not. This produces a large difference in the results as shown in Table 1.

Table 1.
Effect of Mercuric Chloride on Bromine Number

Sample Number	Bromine Number With $HgCl_2$	Bromine Number Without $HgCl_2$
1	102.4	77.0
2	0.7	0.3
3	41.7	30.7
4	8.4	3.0
5	4.3	1.6

Other differences between the methods appear to be insignificant.

The changes Syncrude Research has made to the ASTM method are:

1. A change in the equipment which retains the functional aspects of the specified equipment but which automates the analysis.
2. Whereas the ASTM method uses a 50 mV voltage change to identify the end point, the present method selects the inflection point of the titration curve. The latter end point is more easily obtained and more reproducibly defined.
3. Replacement of carbon tetrachloride by 1,1,1-trichloroethane.

The solvent replacement was dictated by the desire to eliminate carbon tetrachloride from the laboratory environment, due to its reported health hazard. This change produces an upward shift in the results as shown in Table 2.

Table 2.
Effect of Replacement of Carbon Tetrachloride by 1,1,1-Trichloroethane on Bromine Number

Sample Number	Bromine Number	
	With CCl_4	With 1,1,1-trichloroethane
1	75.7	84.0
2	0.5	0.6
3	26.0	27.7
4	2.6	3.0
5	1.9	1.9

The small differences between the data without H_gCl_2 in Table 1 and the data with CCl_4 in Table 2 are due to the accumulated effects of other differences between the ASTM and UOP methods, e.g. end point, electrode, and titrant normality.

The change in bromine number due to the change in solvent is accepted in order to eliminate CCl_4 from laboratory use. For interpretative purposes, only data determined using the same solvent is compared.

Interferences: When the bromine number is taken as a measure of bromine-reactive constituents under specified reaction conditions, the analysis is interference free. However, this is not the case if bromine number is taken as a measure of olefinic unsaturation. The data provided by ASTM D 1159 illustrates this point (1) and should be consulted before interpreting results.

Safety Considerations:

1. Acetic acid — a skin and eye irritant. Flammable.
2. Potassium bromide/bromate solution — avoid contact with the skin. Toxic bromine vapours are generated upon heating.
3. Sulfuric acid — extremely corrosive.
4. 1,1,1-Trichloroethane — moderately toxic by inhalation and skin absorption. Contains inhibitor to prevent formation of phosgene on heating.

Apparatus, Reagents, Materials:

1. pH Meter — with millivolt scale, 10 μA polarizing current output, and recorder output.
2. Dual platinum electrode.
3. Potentiometric recorder — with appropriate scale to record the meter output with 0 to −1000 mV input to the pH meter.
4. Autoburette — Radiometer ABU 12 or ABU 13 fitted with a 25 mL burette. Radiometer A/S, Emdrupvej 72, DK-2400 Copenhagen NV, Denmark.
5. Timer — repeat cycle, set to trigger the ABU 12 at 30 second intervals. See Figure 1 for electrical connections and timer design. To adjust the microswitch set the ABU 12 to a speed of 40 with INCREMENTS off. Zero the volume counter, turn the timer on, and observe the volume counter before and after the microswitch has been activated. Adjust the microswitch for an addition of 0.04 to 0.07 mL per switch closure.
6. Magnetic stirrer and stirring bar.
7. Volumetric flasks — 250 and 1000 mL, Class A.
8. Beaker — 250 mL.
9. Iodine flask — 500 mL.
10. Ice bath.

11. Reagents: (all A.C.S. reagent grade where available)
    Acetic acid, glacial.
    Arrowroot starch.
    Methanol.
    Potassium bromate.
    Potassium bromide.
    Potassium iodide.
    Sulfuric acid.
    1,1,1-Trichloroethane.
12. Standard solution — certified I N sodium thiosulfate solution.
13. Analytical balance.
14. Deionized water.

Procedure: Solution Preparation

1. Dissolve 150 g potassium iodide in distilled water and dilute to 1000 mL.
2. A 0.1 N sodium thiosulfate solution is prepared by diluting 25 mL of the certified I N sodium thiosulfate standard to 250 mL.
3. A starch indicator solution is prepared by mixing 1.25 g arrowroot starch with a few mL of hot distilled water to form a paste. Add the paste to 500 mL of boiling distilled water. Allow to cool and decant into a stoppered bottle. This solution has a short shelf life e.g. 2-3 days.
4. Prepare 25 mL of 1:5 sulfuric acid by carefully adding one volume of concentrated sulfuric acid to 5 volumes of distilled water.
5. Prepare a nominal 0.50 N potassium bromide-bromate solution by dissolving 13.92 g of potassium bromate and 51.0 g of potassium bromide, both previously dried, in distilled water and diluting to 1000 mL. Standardization may be performed iodometrically by the procedure specified in ASTM D 1159.
6. Titration solvent is prepared by mixing the following volumes of materials: 714 mL of glacial acetic acid, 134 mL of 1,1,1-trichloroethane, 134 mL of methanol, and 18 mL of 1:5 sulfuric acid solution.

Analysis of Samples

7. Place 100 mL of titration solvent into the titration vessel and either weigh or pipet the appropriate amount of sample into the titration vessel, the size of the sample being chosen from Table 3.

Table 3.
Bromine Number Sample Size

Bromine Number	Sample Size (g)
0 - 10	2 to 1.6
11 - 20	1 to 0.8
21 - 50	0.5 to 0.4
51 - 100	0.2 to 0.1
> 100	0.1 to 0.05

The weight of the sample should be determined to 0.001 g. For samples of high bromine number it is best to weigh ten times the amount of sample specified in Table 3, dilute to 50 mL with toluene, and then use a 5 mL aliquot for the bromine number.

If the hydrocarbon sample separates to form a two phase system, add toluene up to 40 parts of toluene for one part of sample, to render the sample soluble. If the sample does not remain dissolved during the titration the results will be invalid. Highly volatile samples must be cooled in an ice bath before titration.

8. Set the titration vessel on the titration stand, insert the platinum electrodes, start the stirrer, and allow the system to equilibrate. The pH meter and recorder will indicate −800 to −1000 mV for a typical sample.
9. Refill the Autoburette with titrant, zero the volume counter, and set INCREMENTS on at a titration speed of 40. Turn on the cycle timer and recorder. The system will now make 0.10 mL additions at 30 second intervals until the titration is stopped. The recorder will monitor the progress of the titration. Occasionally during the titration the recorder output is marked with the accumulated volume of titrant indicated by the Autoburette volume counter.
10. When the titration is complete, turn off the Autoburette, recorder, timer and magnetic stirrer.

Determination of End Point

11. The equivalence point is found by fitting the titration curve with a straight line in the region of its inflection point and bisecting this line between the points where the titration curve deviates from the straight line. This point of bisection is taken as the equivalence point as shown in Figure 2. The volume delivered at the equivalence point is calculated by linearly interpolating between the titrant volume markings (step 10) on the recorder trace.

Blanks

12. Titration blanks using solvent only must be run periodically. Due to the low blank values which typically occur, e.g. 0.1 to 0.2 mL, use of the Autoburette in the manual mode is recommended.

Calculations: Calculate the bromine number of the sample as:

$$\text{Bromine Number} = \frac{7.99\ N\ (A - B)}{W}$$

where: A = volume of titrant required for the sample, mL
B = volume of titrant required for the blank, mL
N = normality of titrant
W = sample weight, g

Precision: The ASTM D 1159 criteria for repeatability are used to judge the acceptability of data from the present method.

References:

1. ASTM. "Bromine Number of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration." Annual Standards (1976), Part 23, Method D 1159.
2. UOP. "Bromine Number of Petroleum Distillates and Bromine Index of Industrial Aromatic Hydrocarbons." UOP Laboratory Test Methods for Petroleum and its Products, Universal Oil Products Co., Des Plaines, IL.

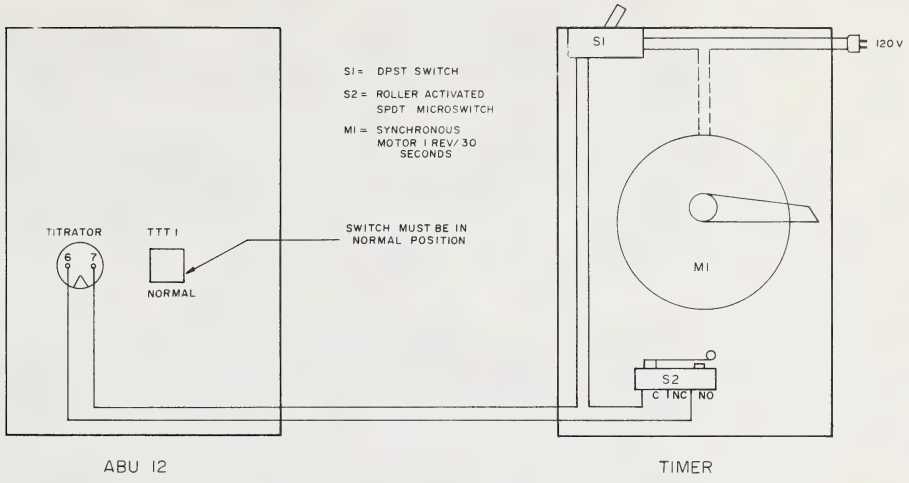


FIGURE 1 TIMER AND ELECTRICAL CONNECTIONS FOR THE AUTOMATED BROMINE NUMBER APPARATUS

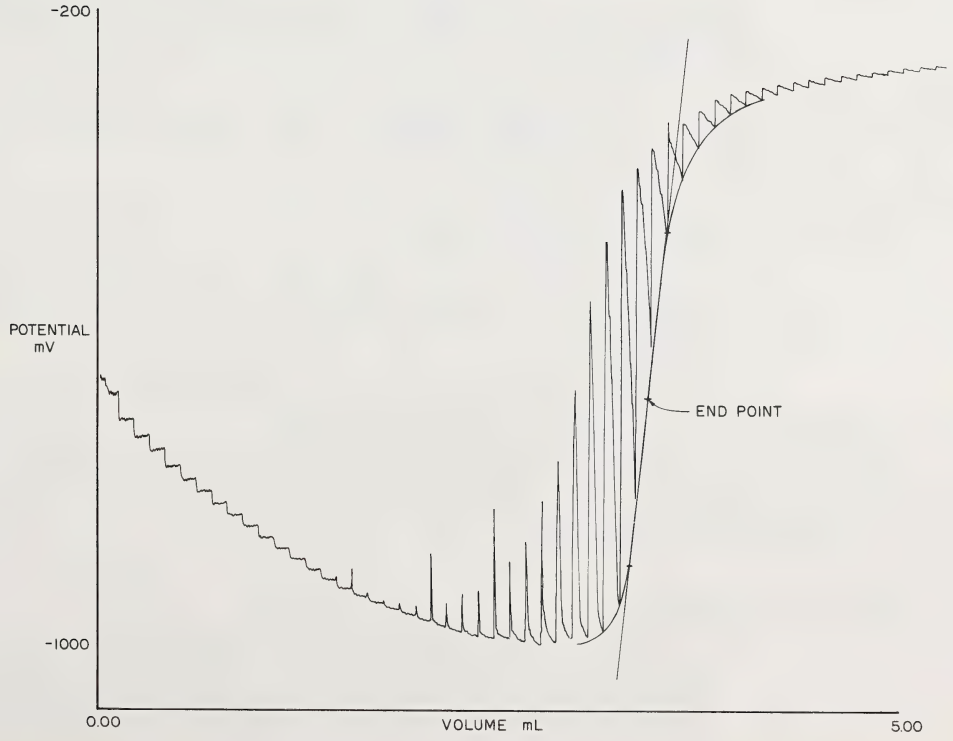


FIGURE 2 TITRATION CURVE FOR A TYPICAL BROMINE NUMBER DETERMINATION

Determination of Sulfur in Liquid Petroleum Hydrocarbons by X-Ray Fluorescence

Scope: This method determines the amount of sulfur in homogeneous liquid petroleum hydrocarbons over the range 0.1 to 6.0 weight percent sulfur. Samples with sulfur contents above this range may be determined after dilution in toluene.

Summary: When a sample is irradiated with a Fe^{55} source, fluorescent x-rays result. The sulfur Kα fluorescence and a background correction at adjacent wavelengths are counted using a Princeton Gamma-Tech Sulfur Analyzer. A calibration of the instrument, wherein the integration time for counting is adjusted such that the displayed signal for the background corrected radiation equals the concentration of the calibration standard, gives a direct readout in % S.

Background: The determination of sulfur with a dedicated x-ray fluorescence analyzer provides a very fast analysis for homogeneous liquid petroleum hydrocarbons. Distillation cuts provide an excellent sample for this method. The method, however, fails for samples that are not homogeneous. For these samples a gravity separation of the solids occurs during the measurement giving rise to time-dependent or biased results.

A small matrix effect occurs due to absorption of the sulfur Kα radiation by the sample matrix. The C/H ratio and density of the sulfur matrix have both been correlated with this attenuation of x-ray fluorescence (1). In practice, matrix effects are minimized by the calibration procedure.

Linear calibrations for this procedure have been established up to the 6 wt % S level. Above this sulfur level a small bias towards low response has been found. This small bias is attributed to the self-absorption of the sulfur Kα radiation.

Interferences: Interfering elements include aluminum, silicon, phosphorus, chlorine, argon, and potassium. Generally the amounts of these elements are insufficient to affect sulfur x-ray counts in samples covered by this method. Atmospheric argon is eliminated by a helium purge.

Safety Considerations: Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.

Apparatus, Reagents, Materials:

1. Princeton Gamma-Tech Model 100 Sulfur Analyzer. Princeton Gamma-Tech, Box 641, Princeton, NJ 08540.
2. X-ray liquid cells, snap-on rings and Mylar film, supplied by Spex Industries Inc., 3880 Park Avenue, Metuchen, NJ 08840. Catalogue no.'s 3515, 3519 and 3517 respectively.
3. Reagents:
   NBS Standard Reference Material SRM 1622, Sulfur in Residual Fuel Oil, nominal concentration 2.14 %S.
   n-Butyl sulfide, bp 182-186°C.
   Paraffin oil, white, with Saybolt viscosity at 37.8°C of 340/355.
   Toluene, A.C.S. reagent grade.
4. Analytical balance.

Procedure: Instrument Startup

1. The Princeton Gamma-Tech sulfur analyzer may be left on continuously. If previously turned off, allow approximately 15 minutes for warmup. Set the MODE control to AUTO and the PRESET to approximately 35 seconds. Increase the helium purge flow until the Mylar film over the sample chamber bulges slightly. If helium flow was previously off, allow to purge for at least one hour.

Calibration

2. Prepare a calibration standard approximating the sulfur content anticipated in the sample in adherence to the following:
   i) National Bureau of Standards SRM 1622 or n-butyl sulfide in paraffin oil are used for samples not requiring dilution. Alternately, a sample of known sulfur content may be used as a calibration standard.
   ii) n-Butyl sulfide in toluene is used for calibration when residue samples or distillates requiring dilution are to be determined.
3. Place a portion of the calibration standard in a sample cup to a depth of about 10 mm. Tear off approximately 50 mm of Mylar film and lay it over the top of the sample cup. Fit a snap-on ring over the cup and press down carefully until it locks the Mylar film into place. Gently pull the edges of the Mylar to eliminate minor wrinkles in the film. Replace film if surface irregularities cannot be alleviated in this manner.
4. Position the sample cup in the instrument with the Mylar side down against the sample window and close the protective cover (a). Press the SHUTTER OPEN button and record four separate readings from the display. If the average reading exceeds the known % S concentration of the calibration standard, decrease the integration time slightly and repeat. Appropriate changes in the integration time may be estimated from the following table.

Difference Between Average Reading & Known Concentration (% S)	Suggested Change In Integration Time (s)
>0.10	1.5
0.10	1.0
0.05	0.5
0.01	0.1

   Repeat the sequence of readings and integration time adjustment until the average of four readings matches the concentration of the standard.
5. Place paraffin oil in a sample cup, cover with Mylar as described above, and measure the average of four readings. Normally a value near 0.00% S is obtained. A significant non-zero reading may indicate insufficient purging, sample leakage, or could otherwise result from replacing the Mylar film in the instrument window assembly. If a non-zero reading is obtained and the former two causes are ruled out, adjust the ZERO screw on the front panel of the instrument to provide a reading of 0.00 ± 0.01 % S.
6. Repeat the calibration procedure until the average of four measurements coincides with the concentration of the standard (b, c).

Sample Preparation and Analysis

7. All liquid samples having a sulfur content of less than 6.0% may be analyzed directly. Transfer the sample to a sample cup to a depth of approximately 10 mm, cover with Mylar film, and seal with a snap-on ring. For samples which may exceed 6.0% S, place approximately 1.0 g of the sample in a tared (nearest mg) 5 mL volumetric flask and weigh. Fill the flask to volume with toluene and weigh again. Transfer the dissolved sample to a sample cup, cover with Mylar and seal.
8. Place the sample cup in the Princeton Gamma-Tech and record the average of four individual readings (d).

Shutdown

9. Depress the SHUTTER OPEN button to close the shutter. If further use of the Princeton Gamma-Tech is not anticipated during the next day, turn off the helium purge flow.

Calculations: For liquid samples requiring no sample preparation, the average of four readings is taken as the percent sulfur. For samples requiring toluene dilution, calculate % S as follows:

$$\% S = \text{Average Reading} \times \frac{\text{Weight Solution}}{\text{Weight Sample}}$$

Precision: Precision estimates for %S in typical bitumen distillation fractions are tabulated below. Data was generated from a total of 12 replicate measurements.

	Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
Naphtha	1.96	±0.017	0.87%
Light Gas Oil	3.00	±0.038	1.27%
Heavy Gas Oil	4.25	±0.036	0.85%
Residue	4.87	±0.027	0.55%

Princeton Gamma-Tech specifies single measurement 95% confidence intervals of ±0.02% at the 0.1% S level, rising to ±0.10% at the 4.0% S level. Precision is improved by a factor of 2 when averaging four measurements. Relative precision is degraded for samples requiring dilution.

Comments:

a. It is essential that a fresh Mylar film be used for every series of replicate measurements. If the Mylar film has been in place for more than 5 minutes, replace with a fresh sheet.

b. Calibration should be performed every day and after every three hours of use.

c. Although each roll of Mylar film is extremely consistent, different rolls do not necessarily have identical properties. Whenever a new roll of Mylar is started, the instrument must be recalibrated using the new film on the standards.

d. If an uncharacteristically high reading is observed, the analysis should be terminated immediately to determine whether the sample cup has leaked. Consult Appendix 5 of the instrument manual for replacement of the Mylar film if leakage has occurred.

Reference:

1. Frechette, G., Herbert, J.C., Thinh, T.P., and Miron, Y.A. "A Better Way to Sulfur Analyses." Hydrocarbon Processing, 54(2), 109-112 (1975).

Determination of Sulfur in Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry

Scope: This method determines the sulfur content of liquid petroleum hydrocarbons with sulfur contents less than about 0.2 wt % and greater than 20 mg/kg. The method may be adapted to determine sulfur at higher concentrations. However other methods are available for these concentration levels, e.g. Method 5.8. For sulfur concentrations below 20 mg/kg the present procedure should be modified to incorporate the syringe injection technique described in Method 5.10.

Summary: Samples with high sulfur contents are diluted with toluene to the 100 mg S/L level. An aliquot is injected into the quartz boat of a single boat inlet and transferred to a combustion tube maintained at 975°C. In the presence of an 80% oxygen/20% argon gas flow, the sample is oxidized. The combustion products are swept into a titration cell where the sulfur dioxide component reacts with the triiodide ion of the electrolyte. The triiodide consumed is coulometrically replaced. The current required to replace the triiodide is a measure of the total sulfur present in the sample. Quantitation is based on comparison with the current required to titrate the sulfur dioxide produced by combustion of an n-butyl sulfide standard (1).

Background: Oxidative microcoulometry has become a widely accepted technique for the determination of low concentrations of sulfur in petroleum products. An excellent recent review has discussed the technical background to the method (2). The phrase oxidative microcoulometry indicates combustion of the sample in an oxygen-rich atmosphere followed by microcoulometric generation of triiodide ion to consume the resultant sulfur dioxide. It is intended to distinguish the technique from reductive microcoulometry which converts sulfur in the sample to hydrogen sulfide which is titrated with coulometrically generated silver ion.

The advantages of oxidative microcoulometry include sensitivity, selectivity, speed, linearity of response and reasonable freedom from interference. Of these advantages sensitivity is the most significant. The concentration range covered by this method is suitable for many samples in which bitumen upgrading has resulted in considerable desulfurization. However the method only covers the intermediate range of the technique's capabilities. The limitation in the sensitivity of the method described here arises from the single inlet which is limited to a maximum sample size of about 5 μL. The injection of larger samples overloads the combustion capacity of the pyrolysis tube. Lower sulfur concentrations can be analyzed by controlling the sample injection rate in order to permit the combustion of a larger sample volume. The injection rate may be controlled by using the syringe injection technique described in Method 5.10 or by using a controlled rate injector (3). For the latter a standard deviation of 20 μg/kg has been reported. The single boat inlet described in the present procedure is convenient since it avoids the direct introduction of a syringe needle into the pyrolysis tube. Furthermore, the single boat inlet is required for samples containing refractory materials.

Interferences: Although sodium azide is included in the electrolyte of the microcoulometric titration to minimize halogen and nitrogen interferences, the method is not applicable when chlorine is present in excess of ten times the sulfur level or nitrogen contents exceed 10%. Heavy metals in excess of 500 mg/kg also interfere (1). A more detailed discussion of these interferences is available elsewhere (2).

Safety Considerations:

1. Acetic acid — a skin and eye irritant. Flammable.
2. Chromic acid — extremely corrosive. A powerful oxidizing agent. Employ rubber gloves and a face shield.
3. Sodium azide — highly toxic. Severe explosion risk when shocked or heated. Irritant to eyes and skin.
4. Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.

Appartus, Reagents, Materials:

1. Dohrmann Microcoulometric Titration System MCTS-30 based on the C-300 microcoulometer and equipped with a single boat inlet sampling accessory and recorder. Dohrmann Division of Envirotech Corp., 3240 Scott Boulevard, Santa Clara, CA 95050.
2. Syringe — 10 μL, equipped with an automatic stop set for 5 μL.
3. Volumetric flasks — 25, 50 and 1000 mL, Class A.
4. Serum bottles — 30 mL, with Viton flange type stoppers and aluminum seals.
5. Reagents:
   Acetic acid, glacial, A.C.S. reagent grade.
   Argon, 99.995%.
   Chromic acid.
   Iodine, 20 mesh or less, A.C.S. reagent grade.
   n-Butyl sulfide, bp 182-186°C.
   Oxygen, 99.99%.
   Potassium iodide, A.C.S. reagent grade.
   Sodium azide, purified.
   Sodium sulfite, A.C.S. reagent grade.
6. Analytical balance.
7. Deionized water.

Procedure:

Electrolyte Preparation

1. Weigh 0.5 g potassium iodide and 0.6 g sodium azide into a 1000 mL volumetric flask and add approximately 900 mL deionized water. Pipet 5 mL of glacial acetic acid into the flask, dilute to volume with deionized water, and mix. Store this electrolyte in a dark area.

Preparation of Standard Solutions

2. Weigh 0.91 g of n-butyl sulfide into a 100 mL volumetric flask. Record the weight to the nearest 0.0001 g. Dilute to volume with toluene and mix. Pipet 5.0 mL of this solution into another 100 mL volumetric flask, dilute to volume with toluene, and mix. Store the standard in a 30 mL serum bottle. The sulfur content of the standard is given by:

   Sulfur (mg/L) = Weight of n-Butyl Sulfide x 109.6

Sample Preparation

3. A weight of sample is diluted to volume with toluene in a volumetric flask to yield a solution containing approximately 100 mg S/L. If the original sample contains less than 100 mg S/L then no dilution is required.

Instrument Settings

4. It is assumed that the MCTS-30 has been installed according to manufacturer's instructions. The instrument parameters are set as follows:

Inlet Furnace Temperature	900°C
Center Furnace Temperature	975°C
Outlet Furnace Temperature	975°C
Bias	155 ± 5 mV
Gain	200
Element Integration	S x 1
Reactant Gas	oxygen, 2.40 mL/s
Carrier Gas	argon, 0.30 mL/s
Auxiliary Gas	argon, 0.30 mL/s

Ensure the GAS SELECTOR VALVE of the single boat inlet directs argon to the pyrolysis tube inlet.

Cell Preparation

5. Remove the cell cap from the titration holder and rinse the electrodes with toluene, acetone, and finally with deionized water.

6. Flush the titration cell several times with fresh electrolyte, allowing the electrolyte to drain from the side arms of the cell. Ensure that all air bubbles are removed from the side arms and close the stopcocks. Fill the cell approximately half full with electrolyte. Position the titration cell so that the magnetic stirrer is rotating smoothly in the middle of the cell.

7. Fit the cell cap into the cell and drain electrolyte through one of the side arms until the level is 10 mm above the platinum electrodes. Adjust the magnetic stirrer to provide a vortex approximately 4 mm in depth. Connect the microcoulometer jacks to the appropriate electrodes.

8. Depress the GEN. READ and BASELINE DISPLAY buttons. The digital readout on the microcoulometer should be negative to indicate that the working electrode would generate titrant. If the readout is positive, flush electrolyte through the cell until a negative value is achieved. If the readout refuses to go negative, add one crystal of sodium sulfite to the stock electrolyte solution and repeat flushing until a negative value is obtained. Depress the SINGLE CYCLE OPERATE button. The microcoulometer will generate titrant, as required, until equilibrium is reached for the bias setting employed. At equilibrium the microcoulometer typically stabilizes at a baseline current offset of approximately −0.5.

9. Attach the capillary inlet of the cell to the exit of the pyrolysis tube. Wrap heating tape around the capillary inlet and reducing joint of the pyrolysis tube. Allow the baseline current offset to restabilize to a value near −2.0. The more negative value of the new baseline corresponds to the requirement that the microcoulometer generate titrant to compensate for the titrant swept from the cell by the gas flow from the combustion tube. Depress the NG. INTEGRATE button and turn on the recorder.

10. Move the quartz boat into the pyrolysis tube and switch the GAS SELECTOR VALVE of the single boat inlet to pass oxygen through the pyrolysis tube inlet. After a few minutes return the GAS SELECTOR VALVE to its normal position where the argon carrier flows through the pyrolysis tube inlet zone and oxygen is directed to the center and exit of the pyrolysis tube. Return the quartz boat to the heat sink of the single boat inlet and then to the sample port. Cycling the boat several times through this sequence will condition the boat to yield a blank value of less than a few nanograms.

    The MCTS-30 is now ready for use.

Analysis of Samples and Standards

11. If the sample boat is in the furnace, retract it to the heat sink and allow the boat to cool for one minute before positioning it under the sample septum. Fill a 10 μL syringe with sample or standard and eliminate any bubbles. Adjust the sample volume to 5 μL using the automatic stop attached to the syringe. Wipe the needle with a Kimwipe. Retract the sample into the barrel of the syringe. Insert the needle through the sample septum and inject the contents of the syringe into the quartz boat. Touch the tip of the needle to the inside of the quartz boat and withdraw the needle from the septum.

12. Depress the START button on the microcoulometer. Slide the boat to a position just inside the carrier gas inlet. When the peak from the volatile components reaches a maximum and begins to fall, slide the quartz boat fully into the pyrolysis tube inlet zone and switch the GAS SELECTOR VALVE to pass oxygen through the pyrolysis tube inlet. Push the CAL/STOP button when the recorder returns to baseline and stabilizes. Record the value displayed on the microcoulometer and subtract a toluene blank to determine the ng S titrated by the microcoulometer for the sample or standard.

13. Move the sample boat to the heat sink to cool for one minute before returning it to a position under the sample septum. Replicate injections are made for each standard and sample to ensure proper syringe technique.

Instrument Shutdown

14. Reduce the furnace temperature to about 700°C. Disconnect the heating tape and allow the capillary inlet to cool. Depress BIAS READ and BASELINE DISPLAY. Turn off the magnetic stirrer. Reduce gas flows to a trickle. Disconnect the cell from the pyrolysis tube.

Calculations:

1. Evaluate the recovery factor, F, for the sulfur standard:

$$F = \frac{A}{5\ C}$$

where: A = nanograms of sulfur titrated by the microcoulometer for the sulfur standard.
C = concentration of sulfur standard in mg/L.

Recovery factors outside the range 0.80 ± 0.10 indicate that the analyzer requires maintenance. The recovery factor is required since both sulfur dioxide and sulfur trioxide are formed on combustion but only the sulfur dioxide reacts with triiodide.

2. For samples requiring dilution the sulfur content is given by:

$$\%\ S = \frac{B}{F} \times \frac{\text{Volume of Diluted Sample (mL)}}{\text{Sample Weight (g)}} \times 2 \times 10^{-5}$$

where: B = nanograms of sulfur titrated by the microcoulometer for the sample.

3. For samples analyzed without dilution the sulfur content is given by:

$$\text{mg S/L} = \frac{B}{5\ F}$$

Precision: Estimates for the precision of results obtained in strict adherence to the described procedure have not been established. Dohrmann application note MC 301 suggests that a relative standard deviation of 3.2% at the 100 mg/L sulfur level can be achieved among replicate determination.

References:

1. Application Note MC-301, "Trace Sulfur Analysis - Oxidative." Dohrmann Envirotech, Santa Clara, CA.
2. Killer, F.C.A. "Microcoulometric Methods For the Determination of Sulfur, Chlorine, Nitrogen and Individual Compounds." Instrument Organic Elemental Analysis, R. Belcher (Ed), Academic Press, 1977.
3. Moore, R.T., Clinton, P., and Barger, V. "Total Sulfur in Hydrocarbons by Oxidative Microcoulometry: 10 ppb to 10%." Paper presented at the 30th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 7, 1979.

Determination of Nitrogen in Liquid Petroleum Hydrocarbons By Chemiluminescence

Scope: This method determines the amount of chemically bound nitrogen in liquid hydrocarbon samples.

Summary: Samples are introduced to the oxygen-rich atmosphere of a pyrolysis tube maintained at 975°C. Nitrogen in the sample is converted to nitric oxide during combustion. The combustion products are dried by passage through $Mg(ClO_4)_2$ before entering the reaction chamber of a chemiluminescence detector. In the detector, ozone reacts with the nitric oxide to form excited nitrogen dioxide.

$$NO + O_3 \longrightarrow NO_2^* + O_2$$

Photo emission occurs as the excited NO_2 reverts to the ground state.

$$NO_2^* \longrightarrow NO_2 + h\nu$$

The emitted light is monitored by a photomultiplier tube to yield a measure of the nitrogen content of the sample. Quantitation is based on comparison with the response for carbazole in toluene standards.

Background: The determination of nitrogen in petroleum has been performed by Kjeldahl (1), microcoulometric (2), and Dumas methods. The chemiluminescent method described in this procedure is the most recent technique applied to nitrogen analysis for petroleum (3-6).

Two injection techniques are described: the automatic boat inlet, and the syringe injection techniques. The automatic boat inlet is used for all samples above about 20 mg N/L, while the syringe injection technique is used for nitrogen contents below this level.

Interferences: The predominant classes of nitrogen compounds in petroleum display equivalent responses. Azo compounds, however, yield low conversion to nitric oxide on combustion.

Safety Considerations:

1. Magnesium perchlorate — a powerful oxidizing agent. A fire and explosion hazard. Irritant to the skin.
2. Ozone — highly toxic by inhalation. A strong irritant to the eyes and upper respiratory tract. The analyzer includes an internal activated carbon trap to deactivate the effluent ozone, and gases from the analyzer are vented.
3. Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.

Apparatus, Reagents, Materials:

1. Dohrmann DN-100 Total Nitrogen Analyzer, Dohrmann Division of Envirotech Corp, 1062 Linda Vista Ave., Mountview, CA 94040.
2. Syringe — 10 μL capacity equipped with an automatic stop set for 5 μL.
3. Volumetric flasks — 5, 25, and 100 mL, Class A.
4. Serum bottles — 30 mL capacity, with Tuf-Bond discs and aluminum seals.
5. Syringe — Hamilton No. 705, 50 μL capacity, equipped with repeating dispenser PB 600-1 and special order needle 75 mm in length.

6. Reagents:
   Activated carbon, pellets.
   Carbazole, mp 244-246°C.
   Cupric oxide, certified A.C.S. wire.
   Helium, 99.995%.
   Magnesium perchlorate.
   Oxygen, 99.995%.
   Toluene, A.C.S. reagent grade.
7. Analytical balance.

Procedure: Preparation of Standard Nitrogen Solution

1. Prepare a nitrogen standard by weighing (to 0.0001 g) approximately 0.119 g carbazole. The carbazole is dissolved in toluene and diluted to 100 mL. The use of some acetone may facilitate dissolution. The standard is stored in a 30 mL serum bottle.

   Nitrogen (mg/L) = Wt Carbazole (g) x 837.9

   A 10 mg N/L standard is prepared by diluting a 10 mL aliquot of the above standard to 100 mL with toluene (a).

Samples Preparation

2. Samples with high nitrogen contents are dissolved in toluene to yield a solution with 50-100 mg N/L. Samples containing less than 100 mg N/L are diluted 1:1 in toluene. Record the sample weight and the total volume of solution for use in the calculations.

   Samples at the 1 mg N/L level are analyzed without dilution (b).

A. Automatic Boat Inlet Procedure

Instrument Parameters

3.

Inlet Temperature	Approx. 850°C
Center Temperature	Approx. 975°C
Outlet Temperature	Approx. 975°C
Function	Boat Operate
Meter Range	x 10
Integration Time	180 s
Calibrate	ppm
Reactant Gas	Oxygen, 4.20 mL/s
Carrier Gas	Helium, 0.13 mL/s
Auxiliary	Helium, 0.20 mL/s
Purge	Helium, 3.30 mL/s
Ozonator	Oxygen, 1.50 mL/s

The method assumes that the instrument has been set up in accordance with manufacturer's specifications and left in the standby configuration. In this configuration the oxygen flow is turned off at the regulator line valve and the helium pressure is set to allow helium to trickle through the combustion tube.

Startup Procedure

4. From the standby configuration, ensure that the operating furnace temperatures listed above are established. Ensure that sufficient gases are present for the day's operation. The presence of leaks may be detected by subjecting the detector effluent to a 200 mm of water back pressure. Failure of the standby helium flow to overcome the back pressure indicates the presence of a leak which should be corrected.

   Increase the pressure delivered by the helium regulator to give the flows listed in step 3. Turn on the oxygen flow at the regulator line valve. After about 1 minute turn the OZONE switch on. Cycle the DN-100 through 3 cycles by pressing the START button when the READY light comes on. Initial readings will be high, but they should stabilize to less than 10 ng N. The ozonator may be damaged in the absence of oxygen flow.

Analysis of Samples and Standards

5. Fill the 10 μL syringe with toluene and eliminate all bubbles. Depress the plunger to the automatic stop set for 5 μL. Wipe the outside of the needle with a Kimwipe. Retract the plunger to position the sample in the barrel of the syringe. Insert the needle through the sample septum and inject the contents of the syringe into the platinum boat. Touch the tip of the needle on the inside of the boat and then withdraw from the septum. Press START to initiate the analysis sequence (c). Repeat the blank to obtain an average value. The blank should be less than 15 ng N.

   Flush the analysis syringe several times with the standard. Using the analysis syringe, analyze the 5 μL volume of carbazole standard delivered by the automatic stop. If the measured concentration of nitrogen is significantly different from the concentration of nitrogen injected, release the lock on the CALIBRATE vernier, press the CALIBRATE button, and adjust the reading to correspond to the blank plus the nitrogen content of the standard. Now record replicate determinations of the standard (c).

   For samples, replicate determinations with the 5 μL sample volume should be performed to ensure against errors in syringe technique (c). Flush the analysis syringe several times with sample before taking the sample.

Instrument Shutdown

6. Turn the center and outlet furnace controls to settings corresponding to approximately 800°C. The inlet furnace control may be left at its normal setting. Turn the OZONE switch off. Turn off the oxygen supply at the regulator line valve. Reduce the helium pressure to 35 kPa(g) at the regulator. The helium pressure should be monitored for several minutes to ensure that it has stabilized (d, e).

B. Syringe Injection Procedure

Instrument Parameters

7.

Inlet Temperature	Approx. 750°C
Center Temperature	Approx. 975°C
Outlet Temperature	Approx. 975°C
Function	Direct Operate
Meter Range	x 10
Integration Time	390 s
Calibrate	ng
Reactant Gas	Oxygen, 4.20 mL/s
Carrier Gas	Helium, 0.80 mL/s
Auxiliary Gas	Not Applicable
Purge	Not Applicable
Ozonator	Oxygen, 150 mL/s

   The method assumes the instrument has been set up in accordance with manufacturer's specifications and left in the standby condition. In this condition the oxygen flow is turned off at the regulator line valve and the helium pressure is set to allow helium to trickle through the combustion tube.

Startup Procedure

8. From the standby configuration, ensure that the operating furnace temperatures listed above are established. Ensure that sufficient gases are present for the day's operation. The presence of leaks may be detected by subjecting the detector effluent to a 200 mm of water back pressure. Failure of the standby helium flow to overcome the back pressure indicates the presence of a leak which should be corrected before proceeding.

   Increase the pressure delivered by the helium regulator to give the flows listed in step 7. Turn on the oxygen flow at the regulator line valve. Switch the oxygen and helium input lines to the pyrolysis tube for 5 minutes and then return to the

normal configuration. Turn the OZONE switch on. The ozonator may be damaged in absence of oxygen flow.

Analysis of Samples and Standards

9. Insert the needle of the 50 μL syringe through the pyrolysis tube septum to obtain a needle blank (f). Repeat the needle blank to obtain a second value. Duplicate values should not differ by more than a few ng. Average the duplicate values to obtain the needle blank.

   Fill the syringe with toluene and eliminate all air bubbles. Depress the push button on the repeating dispenser to eject toluene until the 30 μL mark is reached. Wipe the needle with a Kimwipe and insert the syringe needle into the septum of the pyrolysis tube (d). Push the START button on the DN-100 and inject the toluene blank at a rate of approximately 0.5 μL/s. Repeat the toluene blank to obtain a second value. Duplicate values should not differ by more than a few ng. Average duplicate values to obtain the toluene blank.

   Flush the syringe several times with the 10 mg N/L standard. Fill the syringe with the standard and determine the response using the injection technique described for the toluene blank. As before, a duplicate value differing by less than a few ng N is obtained and the average response of the standard is calculated. The detector output should be monitored between injections to ensure that the detector has returned to baseline.

   Flush the syringe several times with the sample. Fill the syringe with the sample and determine the response using the injection technique described for the toluene blank. Duplicate values differing by less than a few ng N are obtained and the average response for the sample is calculated. The detector output is monitored between injections to ensure that the detector has returned to baseline.

Instrument Shutdown

10. Turn the center and outlet furnace controls to settings corresponding to approximately 800°C. The inlet furnace control may be left at its normal setting. Turn the OZONE switch off. Turn off the oxygen supply at the regulator line valve. Reduce the helium pressure to allow helium to trickle through the combustion tube. The helium pressure should be monitored for several minutes to ensure that it has stabilized (d, e).

Calculations:

A. Automatic Boat Inlet Procedure

1. The syringe factor, F, is calculated as:

$$F = \frac{C}{S - B}$$

   where: C = nitrogen concentration of the calibration standard in mg/L
   S = average DN-100 response for the calibration standard
   B = average toluene blank

2. The nitrogen concentration of the injected solution, A, in mg/L is:

$$A = F(V - B)$$

   where: F = syringe factor
   V = average DN-100 response for the sample
   B = average toluene blank

3. The nitrogen concentration of the sample is given by:

$$\text{mg N/kg} = A \times \frac{\text{Volume of Diluted Sample (mL)}}{\text{Sample Weight (g)}}$$

B. Syringe Injection Procedure

1. The syringe factor, F, is calculated as:

$$F = \frac{C}{S - B}$$

where: C = nitrogen concentration of the calibration standard in mg/L
S = average DN-100 response for the calibration standard
B = average toluene blank

2. The nitrogen concentration of the injected solution, A, in mg/L is:

$$A = F(V - D)$$

where: F = syringe factor
V = average DN-100 response for the sample
D = average needle blank

3. For undiluted samples the nitrogen content may be reported as:

$$\text{mg N/kg} = \frac{A}{\text{Sample Density}}$$

For diluted samples the nitrogen content may be reported as:

$$\text{mg N/kg} = A \times \frac{\text{Volume of Diluted Sample (mL)}}{\text{Sample Weight (g)}}$$

Precision: Precision evaluations for the repeatability of nitrogen determinations on samples of bitumen and related materials have not been undertaken. The following data, based on 9 injections of a carbazole in toluene standard solution, is considered typical:

Mean Value (mg N/L)	Standard Deviation (mg N/L)	Relative Standard Deviation
100.14	±0.51	0.50%

The manufacturer quotes the precision of a nitrogen analysis to be ±0.2 mg N/L or 2% relative, whichever is greater.

Comments:

a. A new carbazole standard should be prepared approximately every ten days.

b. For new sample types analyzed without dilution, it is recommended that the syringe factor C/(S − B) described in the calculations be determined for the sample matrix. The method assumes that the syringe factor is the same for the sample and toluene matrices.

c. After injecting the sample and removing the needle from the sample septum, the START button should be pressed as soon as possible.

d. In the automatic boat inlet configuration the $Mg(ClO_4)_2$ drying agent should be changed after 16 hours of use. In the syringe injection mode the $Mg(ClO_4)_2$ is replaced every 2 to 3 hours.

e. Renewal of the sample septum is recommended after 50 injections in the automatic boat mode and after 25 injections in the syringe mode.

f. Avoid contact between the syringe needle and walls of the pyrolysis tube.

References:

1. Bradstreet, R.B. The Kjeldahl Method for Organic Nitrogen. Academic Press, New York, 1975.

2. ASTM. "Trace Nitrogen in Liquid Petroleum Hydrocarbons (Microcoulometric Method)." Annual Standards (1976), Part 25, Method D 3431.

3. Drushel, H.V. Anal. Chem. 49, 932 (1977).

4. Parks, R.E. "Analysis for Chemically Bound Nitrogen Using Pyro-Chemiluminescence." Paper presented at the 27th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 2, 1976.

5. Castro, J.M., and Moore, R.T. "Total Nitrogen in Hydrocarbons by Automated Chemiluminescence Detection System: 20 ppb to 1%." Paper presented at the 30th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 7, 1979.

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Determination of Nickel, Iron and Vanadium in Gas Oil Samples by Inductively Coupled Argon Plasma Emission Spectroscopy Preceded by Wet Ashing

Scope: This method determines the nickel, iron and vanadium content of gas oil samples in the range from 0.1 mg/kg to 100 mg/kg.

Summary: A 10 g sample of gas oil is charred with sulfuric acid and subsequently ashed. The resulting sulfates are then converted to their corresponding chloride salts to ensure complete solubility. A barium internal standard is added to the sample which is analyzed with an inductively coupled argon plasma emission spectrometer (I.C.A.P.).

Background: The analysis of samples of oil for Ni, Fe, and V present two basic problems. The most serious is the fact that these metals are partly or totally in the form of volatile chemically stable porphyrin complexes. Extreme conditions are needed to destroy the complexes, yet if conditions are excessive the metal will be lost through volatilization of the complex. The second problem is that the alternate direct aspiration of the sample introduces large quantities of carbon into the plasma. This carbon causes marked and somewhat variable background changes in all direct measurement techniques.

The present method utilizes a sample preparation developed for X-ray fluorescence and the superior detection of the I.C.A.P. The method is extremely technique sensitive in the sample preparation stage. Further background on the I.C.A.P. may be found in Method 2.3.

Safety Considerations:

1. I.C.A.P. — avoid direct exposure to the high intensity ultraviolet light produced by the plasma. Appropriate precautions are required in dealing with the very high voltages in the plasma generator.
2. Hydrochloric acid — highly toxic by inhalation. A strong irritant to the eyes and skin.
3. Sulfuric acid — extremely corrosive.

Apparatus, Reagents, Materials:

1. Inductively coupled argon plasma spectrometer (a) — Jarrell-Ash Model 96-986 with detectors for Ba, Ni, V, and Fe. Jarrell-Ash Division, Fisher Scientific Co., 590 Lincoln St., Waltham, MA 02154.
2. Pump (b) — Gilson Minipuls model MPI with 0.63 mm ID polyvinyl chloride manifold tubing. Gilson Medical Electronics Inc., P.O. Box 27, 3000 West Beltline Highway, Middleton, WI 53562.
3. 1 mL micropipet — Oxford P-7000 sampler with tips.
4. Crucibles — 100 mL Vycor.
5. Graduated cylinders — 10 and 100 mL.
6. Volumetric flasks — 100 and 1000 mL, Class A.
7. Hot plate.
8. Glass stirring rods.
9. Infrared heat lamp.
10. Pyrex watch glasses.
11. Muffle furnace.
12. Steam bath.
13. Sample vials — 10 mL.
14. Sulfuric acid — A.C.S. reagent grade.

15. Hydrochloric acid — A.C.S. reagent grade.
16. Barium carbonate — 99.999%, Spex Industries Inc., 3880 Park Avenue, Metuchen, NJ 08840.
17. Pure Metals — Vanadium (99.9%), Iron (99.999%), and Nickel (99.99%) also available from Spex Industries.
18. Yttrium solution — 1000 mg/L.
19. Analytical balance.
20. Deionized water.

Procedure: Preparation of stock solutions.

1. Weigh 1.4370 g of barium carbonate and transfer to a 1000 mL volumetric flask. Add approximately 5 mL of concentrated HCl drop by drop, taking care to avoid splattering. After all the barium carbonate has been dissolved, dilute to volume with deionized water. This is a 1000 mg/L barium stock solution. It is very stable.
2. Add 100 mL HNO_3 to 1.000 g Ni metal and heat on a hot plate until all the metal is dissolved. Transfer to a 1000 mL volumetric flask and dilute to volume with deionized water. In a similar manner, prepare stock solutions of Fe and V using HCl and HNO_3 respectively.

Preparation of the Internal Standard

3. Pipet 10 mL of the 1000 mg/L barium stock solution into a 100 mL volumetric flask and dilute to volume with deionized water. This solution is used in the preparation of the samples and the blank.

Preparation of the 10% HCl Solution

4. Add 100 mL of concentrated HCl from a graduated cylinder to a 1000 mL volumetric flask partially filled with deionized water and dilute to volume.

Preparation of Reagent Blank

5. Add 10 mL of concentrated H_2S0_4 from a graduated cylinder to a 100 mL Vycor crucible and place on a hot plate set at high. When no more $S0_3$ fumes can be seen, remove the crucible from the hot plate, cover it with a pyrex watch glass and place it into the muffle furnace at 540°C for 30 min. After the crucible has cooled remove the watch glass and add 10 mL of concentrated HCl by pouring it down the side of the crucible. Evaporate the acid to dryness on a steam bath. When all the acid is evaporated, remove the crucible from the steam bath, cover with a watch glass and allow to cool. Add 10 mL of 10% HCl from a graduated cylinder and 1.00 mL of 100 mg/L barium solution using the micropipet. Replace the cover and heat on the steam bath for 10 min. After the solution has cooled, swirl it around in the crucible and decant into a sample vial. Do not add any water when transferring the reagent blank from the crucible to the vial. It is not necessary to transfer all the solution. The purpose here is to keep the total volume to minimum when the blank is measured.

Preparation of the Standard Solutions

6. Place 10 mL concentrated HCl in a 100 mL volumetric flask. With a micropipet add 1.00 mL of 1000 mg/L barium stock solution. Dilute to volume with deionized water and shake. This blank for the standard is denoted GAS1.
7. Place 10 mL concentrated HCl in a 100 mL volumetric flask. With a micropipet add 1.00 mL of the 1000 mg/L stock solutions of barium, iron, nickel and vanadium. Dilute to volume with distilled water and shake. This standard solution is denoted GAS2.

Sample Preparation

8. Accurately weigh 10 g of sample into a 100 mL Vycor crucible. Add 10 mL of concentrated H_2SO_4 and place on a hot plate set at high. Stir the mixture with a glass rod until the gas oil is charred. When the reaction has subsided, place an infrared heat lamp about 100 mm above the crucible and turn it on. When no more $S0_3$ fumes can be seen, remove the crucible from the hot plate, cover it with a pyrex watch glass and place it into the muffle furnace at 540°C until the sample is completely ashed. Usually a sample will take 6 to 10 hours to ash completely. After the sample has cooled, add 10 mL of concentrated HCl by pouring it down the sides of the crucible. Evaporate the acid to dryness on a steam bath. Remove the crucible and let it cool. Add 10 mL of 10% HCl and 1.00 mL of 100 mg/L barium solution with the micropipet. Cover the crucible with a watch glass and place on a steam bath for 10 minutes. After cooling, swirl the solution and decant it into a sample vial. Do not add any water when transferring the sample. It is not necessary to transfer all of the solution. The purpose here is to keep the total volume to a minimum.

Analysis of Samples and Standards on the I.C.A.P.

9. Since the I.C.A.P. conditions are dependent upon the nebulizer in use, set up the instrument to the normal operating conditions for aqueous samples. This information is recorded for each nebulizer in the I.C.A.P. data book (c). Typical conditions are:

Power	1.15 kW
Observation height	17 mm above coil
Nebulizer pressure	140 kPa(g)
Coolant Gas	330 mL/s argon
Plasma Gas	33 mL/s argon to light
	17 mL/s argon to operate
Sample Gas	No flow to light
	10 mL/s argon to operate
Sample Uptake (b)	13 μL/s

When properly adjusted, the red emission tip produced by a 1000 mg/L Yttrium solution should be 10 mm below the entrance slits.

Call up Matrix "GAOL". A copy of the matrix (c) is shown in Figure 1.

Aspirate each of the standards using 3 burns each, with an "EGGGN" command. Standardize, and check the GAS2 standard for correct analysis (10.0 mg/L of each metal).

Measure each sample. Check standard GAS2 after each 5 samples.

Calculations: Concentrations of iron, nickel, or vanadium are given by:

$$\text{mg/kg Fe, Ni, or V} = \frac{\text{Concentration of Fe, Ni, or V from I.C.A.P. (mg/L)} - \text{Blank}}{\text{Sample Weight (g)}} \times 10$$

Precision: Typical precision data associated with Ni, Fe, and V determinations on gas oil samples by I.C.A.P. are tabulated below. Values were generated from 6 replicate sample determinations conducted as described in this procedure.

	Mean Value (mg/kg)	Standard Deviation (mg/kg)	Relative Standard Deviation
Ni	0.14	±0.08	57.1%
Fe	5.86	±0.38	6.5%
V	0.007	±0.002	28.6%

The repeatability of this analysis is highly dependent on the skill of the operator, particularly as it relates to the sample pretreatment and dissolution steps.

Comments:

a. The instrument fully described in Method 2.3 may be used in this method without modification. The previous method incorporates extra equipment not needed for this procedure.

b. While use of the pump is optional for most nebulizers, it has been found to greatly reduce operating problems caused by minor variations in nebulizer performance.

c. See the comments with Method 2.3.

```
 PR
MX NAME: GAOL
MX NAME: GA
# OF LCN'S:  4  # OF SM'S:  1
MODE:CN
FORMAT:  1  1  3
IS# 1
IS# 2
IS# 3
IS# 4
STD# 1  GAS1
STD# 2  GAS2
STD# 3
STD# 4
STD# 5

 1 BK 15  1  *  1  Ø  4  1          Ø .1162     Ø -.131  .1255
 2 NI 18  1  1  2  1  4  1 NIGO 1.58Ø .7416 .1841 1.275 -.Ø71
 3 FE  5  1  1  2  1  4  1 FEGO .592Ø 2.2Ø6 .Ø688 .1761 -.ØØ2
 4 V  1Ø  1  1  2  1  4  1 VVGO .5182 2.111 .Ø6Ø2 .8791 .ØØ29

CURVE NAME :NIGO
5.57495 1ØØ.ØØØ
      Ø       Ø
CURVE NAME :FEGO
21.3717 1ØØ.ØØØ
      Ø       Ø
CURVE NAME :VVGO
2Ø.5Ø78 1ØØ.ØØØ
      Ø       Ø

SM NAME:OL PRTY:  2
 1 1.ØØØ
 2 1.ØØØ
 3 1.ØØØ
 4 1.ØØØ
#
```

FIGURE 1. PRINTOUT OF MATRIX GAOL

N.L.C. - B.N.C.
3 3286 10664889 8